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GIVING THE

# NOMENCLATURE AND SYSTEM OF NOTATION

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1. Before beginning to write an abstract, it is desirable to read through the whole of the original paper, in order to form a judgment as to its importance, and as to the scale on which the abstract should accordingly be made.

2. The abstract should mainly consist of the expression, in the abstractor's own words, of the substance of the paper.

3. The abstract should be made as concise as possible, consistently with a clear and accurate statement of the author's results or theories, due regard being paid to their import.

4. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should as a rule be made of this fact. Important references to the researches of others quoted by an author should be reproduced in the abstract. Always employ figures instead of Roman numerals for references, thus:—*Annalen*, **221**, 92, instead of ccxxi, 92.

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6. As a rule, details of methods of preparation or analysis, or generally speaking of work, may be omitted, unless such details are essential to the understanding of the results, or have some independent value.

### Nomenclature.

7. Employ names such as *sodium chloride*, *potassium sulphate*, *ethyl acetate*, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chloride, sulphurous and sulphuric acid.

8. Term compounds of metallic and alcoholic radicles with the group OH, *hydroxides* and not hydrates; for example, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallization. Compounds such as $CH_3ONa$, $C_2H_5ONa$, $C_7H_{15}ONa$, &c., should be termed sodium methoxide, ethoxide, heptyloxide, &c.

9. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as $HNO_3$, $H_2SO_4$, $H_3PO_4$, and denote the oxides which form acids by names such as sulphuric anhydride, carbonic anhydride. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen sodium sulphate, hydrogen disodium phosphate, &c., to the acid salts. Basic salts are as a rule best designated merely by their *formulæ.*

10. Use names such as *methane*, *ethane*, &c., for the normal paraffins or hydrocarbons of the $C_nH_{2n+2}$ series of the form $CH_3{\cdot}[CH_2]_5{\cdot}CH_3$, &c. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane; for example, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 =$ propylmethane; $CH_3{\cdot}CH(CH_3)_2 =$ isopropylmethane or trimethylmethane; or, although less frequently, by names such as diisopropyl.

11. Term the hydrocarbons $C_2H_4$ and $C_2H_2$ *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethylene, &c., denoting the di-derivatives of the form $C_nH_{2n+1}{\cdot}CH{:}CH{\cdot}C_nH_{2n+1}$ as $\alpha$-, and those of the form $CH_2{:}C(C_nH_{2n+1})_2$ as $\beta$-compounds, thus: $CH_3{\cdot}CH{:}CH{\cdot}CH_3 =$ $\alpha$-dimethylethylene; $CH_2{:}C(CH_3)_2 = \beta$-dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH{:}C{\cdot}C_nH_{2n+1}$ and $C_nH_{2n+1}{\cdot}C{:}C{\cdot}C_nH_{2n+1}$. Adopt the same *allene* for the hydrocarbon $CH_2{:}C{:}CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

12. Distinguish all alcohols, that is, hydroxyl-derivatives of hydrocarbons, by names ending in *ol*; such as quinol, catechol, resorcinol, saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol: furfuraldehyde instead of furfurol; fucusaldehyde instead of fucusol. Ethers derived from phenols, such as $C_6H_5{\cdot}OCH_3$, &c., hitherto called anisol, anethol, &c., may be distinguished by names ending in *oïl*, as anisoïl and anethoïl.

Alcohols should be spoken of as mono-, di-, tri-, or n-*hydric*, according to the number of OH groups.

13. Compounds analogous to the acids of the lactic series containing the group OH should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups $C_2H_5O$, $C_6H_5O$, $CH_3{\cdot}COO$, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus

ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen-atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2{\cdot}COOH$, and not $C_6H_3(OC_2H_5)_2{\cdot}COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2{\cdot}COOH$.

14. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 12).

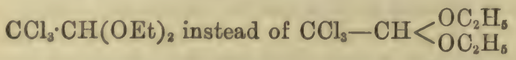
15. Compounds of the radicle $SO_3H$ should, whenever possible, be termed *sulphonic* acids, or failing this, *sulpho-compounds*: as benzenesulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2{\cdot}NH_2$ should be termed sulphonamides.

16. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

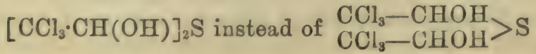
## Notation.

17. Equations should *be omitted* unless essential to the understanding of the results; they, as a rule, should *not* be written on a separate line, but should "run on" with the text.

18. To economise space, it is desirable: 1, that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; 2, that formulæ should be shortened by the judicious employment of the symbols Me for $CH_3$, Et for $C_2H_5$, $Pr^{\alpha}$ for $CH_2{\cdot}CH_2{\cdot}CH_3$, $Pr^{\beta}$ for $CH(CH_3)_2$, Ph for $C_6H_5$, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$; and 3, that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:



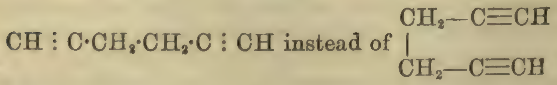
$CCl_3{\cdot}CH(OEt)_2$ instead of $CCl_3{-}CH{<}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$



$[CCl_3{\cdot}CH(OH)]_2S$ instead of $\begin{matrix}CCl_3{-}CHOH\\CCl_3{-}CHOH\end{matrix}{>}S$

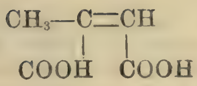
$CH_2 : CH_2$ instead of $CH_2{=}CH_2$

$CH \vdots CH$ instead of $CH{\equiv}CH$

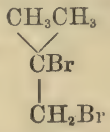


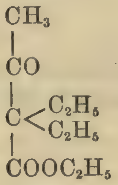
$CH \vdots C{\cdot}CH_2{\cdot}CH_2{\cdot}C \vdots CH$ instead of $\begin{matrix}CH_2{-}C{\equiv}CH\\ |\\ CH_2{-}C{\equiv}CH\end{matrix}$

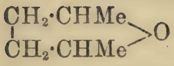
$CHMe : CHPr^{\alpha}$ instead of $CH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$

$COOH{\cdot}CH : CMe{\cdot}COOH$ instead of 

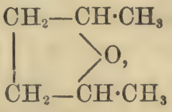
$$\begin{array}{ccc} CH_3— & C{=}CH & \\ | & | & \\ COOH & COOH & \end{array}$$

$CH_2Br{\cdot}CBrMe$ instead of 

$CEt_2Ac{\cdot}COOEt$ instead of 

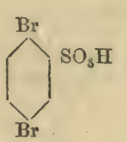


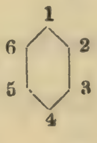
$$\left.\begin{array}{l} CH_2{\cdot}CHMe \\ | \\ CH_2{\cdot}CHMe \end{array}\right> O$$

instead of 

$CHPh(OBz){\cdot}CH(OBz){\cdot}COOEt$ instead of
$C_6H_5{\cdot}CH(O{\cdot}CO{\cdot}C_6H_5){\cdot}CH(O{\cdot}COC_6H_5){\cdot}COOC_2H_5$.

19. In representing the constitution of benzene-derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, for example:—

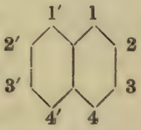
Paradibromobenzenesulphonic acid, $C_6H_3Br_2{\cdot}SO_3H[Br : SO_3H : Br = 1 : 2 : 4]$ instead of  the figures always being used in

the order 

Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as 1 : 2 dibromobenzene, 1 : 3 dibromobenzene, &c., rather than by terming them ortho- or meta-dibromobenzene, &c.

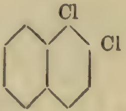
20. Moreover, in representing the constitution of derivatives of other "closed-chain" hydrocarbons do not, as a rule, employ graphic formulæ, but merely indicate the position of the radicles introduced in the following manner:—

*In the case of naphthalene*, express the position of the radicles introduced in place of hydrogen relatively to the carbon-atoms common to the two "rings," and number the positions in the one ring 1, 2, 3, 4, and those in the other 1′, 2′, 3′, 4′ in the order shown by the annexed symbol:—

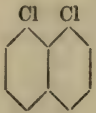


The dichloronaphthalenes, for example, are spoken of simply as 1 : 2 dichloronaphthalene, or dichloronaphthalene[Cl : Cl = 1 : 2], &c., thus:—

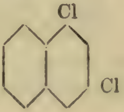
1 : 2 dichloronaphthalene =



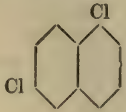
1 : 1′ dichloronaphthalene =



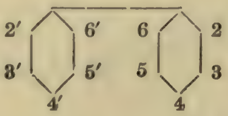
1 : 3 dichloronaphthalene =



1 : 3′ dichloronaphthalene =



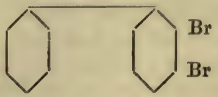
*In the case of diphenyl*, indicate the position of the radicles relatively to the carbon-atom of one $C_6$ group which is associated with the other $C_6$ group, and number the positions in the one group by the figures, 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2′, 3′, 4′, 5′, 6′. as shown by the following symbol:



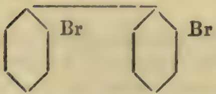
Thus the mono-derivatives, the bromodiphenyls, for example, are represented as

Bromodiphenyl [Br = 2]
" [Br = 3]
" [Br = 4]

and the two dibromodiphenyls

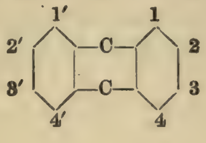


and



are respectively dibromodiphenyl [Br : Br = 2 : 3] and dibromodiphenyl [Br : Br = 2 : 6′].

*In the case of anthracene*, employ the following symbol, and indicate the position of the radicles relatively to the central $C_2$-group:



Examples:

Alizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 2].
Quinizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 4].
Anthraflavic acid, $C_6H_3(OH) : C_2O_2 : C_6H_3(OH)$ [OH : OH = 2 : 3′].

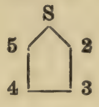
Purpurin, $C_6H_4 : C_2O_2 : C_6H(OH)_3$ [OH : OH : OH = 1 : 2 : 4].

In speaking of compounds such as these, their constitution may be represented by the names

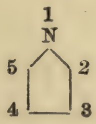
1 : 2 Dihydroxyanthraquinone = Alizarin.
1 : 4 ,, = Quinizarin.
2 : 3′ ,, = Anthraflavic acid.
1 : 2 : 4 Trihydroxyanthraquinone = Purpurin.

Always include the letters and figures indicating the constitution of derivatives of closed-chain hydrocarbons in square brackets.

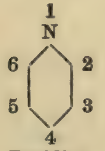
21. *In the case of thiophen*, express the position of the radicles introduced relatively to the sulphur-atom by numbers, as shown by the following symbol:



*In the cases of pyrroline and pyridine*, indicate the position relatively to the nitrogen-atoms as shown by the following symbols:

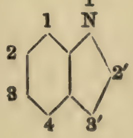


Pyrroline.

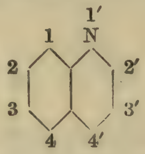


Pyridine.

In the case of indole, positions should be numbered as shown in the following symbol:—



In the case of quinoline, express the positions relatively to the carbon-atoms common to the two rings, and number the positions in the carbon ring 1, 2, 3, 4, and those in the nitrogen ring 1′, 2′, 3′, 4′ in the order shown by the annexed symbol :—



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# JOURNAL

OF

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## ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## PART I.

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## Organic Chemistry.

**Elementary Composition of the Mineral Oils.** By CARL ENGLER and L. JEZIORANSKI (*Ber.*, 1895, **28**, 2501—2505).—The authors have made analyses of samples of oil from Galicia, Sumatra, Baku (Bibi-Eibat), Alsace (Pechelbronn), and Pennsylvania, and also of the various fractions obtained from these oils, namely, below 150°, 150—200°, residue. From the analyses, and from the amount of each fraction absorbed by concentrated sulphuric acid, the authors conclude that the lower fractions consist mainly of saturated hydrocarbons of the paraffin series, except in the case of the Baku oil, whereas the portion boiling above 200° consists, in all cases, mainly of unsaturated hydrocarbons of the olefine series. J. J. S.

**Fractional Distillation applied to American Petroleum and Russian Kerosene.** By J. ALFRED WANKLYN and WILLIAM J. COOPER (*Phil. Mag.*, 1895, [5], **40**, 225—228).—The paper contains the results of the authors' experiments on the fractional distillation of American petroleum, and the vapour density, specific gravity, and composition of the various fractions, the results being compared with those obtained by the authors in the case of Russian kerosene. They consider that each of these petroleums contains a homologous series of hydrocarbons with a common increment of 7, instead of 14, a result that would require the accepted atomic weight of carbon to be halved. For a like carbon contents, the hydrocarbons of the Russian series, which contain 2 atoms of hydrogen less per molecule, always show a slightly greater specific gravity, the increment varying from 0·025 to 0·035. L. M. J.

**Russian Kerosene.** By J. ALFRED WANKLYN and WILLIAM J. COOPER (*Chem. News*, 1895, **72**, 7).—A tabular *résumé* is given of the work done on the hydrocarbons existing in commercial Russian kerosene (Abstr., 1895, i, 77 and 437). D. A. L.

**Hexylene and Hexylic Hydride derived from Mannitol by Reduction with Hydriodic acid.** By J. ALFRED WANKLYN (*Chem. News*, 1895, **72**, 75).—The specific gravity of hexylene at 0° is given as 0·7017, and of hexylic hydride at 0° as 0·6759, differing by 0·0258. A similar difference, of 0·025 to 0·035, is observed between the densities of the hydrocarbons of the same carbon condensation obtained from Russian and American petroleums respectively, the former being the denser. D. A. L.

**Unsaturated Hydrocarbons.** By ALEXANDRE DESGREZ (*Ann. Chim. Phys.*, 1894, [7], **3**, 209—246).—Berthelot (*Ann. Chim Phys.*, [3], **43**, 385, and [5], **23**, 184) has shown that unsaturated hydrocarbons can be made to combine with the elements of water indirectly by means of sulphuric acid; and Béhal and Desgrez (Abstr., 1892, 1162) have shown that unsaturated hydrocarbons also unite with the elements of acetic acid at a fairly high temperature to form ethereal salts. The author now demonstrates that the elements of water can be directly added to the hydrocarbons of the acetylene series. For this purpose, the hydrocarbon is placed with water in iron tubes, enamelled inside, and heated in a bath of sodium and potassium nitrates. Instead of acetylene, the author has used acetylenedicarboxylic acid, and finds that, when the acid and water are heated at 315° for 20 minutes, a quantity of paraldehyde is formed. Tetrolic acid, when heated with water in a similar manner, gives rise to acetone.

Œnanthylidene, with water at 325°, yields methyl amyl ketone. Caprylidene, when heated with water for three hours at 320—330°, yields methyl hexyl ketone. Phenylacetylene, under similar conditions, gives acetophenone; methylbutylacetylene yields a mixture of equal quantities of methyl amyl ketone and *ethyl butyl ketone*. The ketone distils at 146—147°, and does not unite with sodium hydrogen sulphite. A number of experiments were made with methylamylacetylene and water, from which the author concludes that the yield of ketone increases with the period of heating, that a maximum is reached with a period of three hours, from which point the yield again decreases, and, further, that the yield increases with the temperature, reaching a maximum of 75 per cent. of the theoretical at 360°. The product consists of a mixture of methylamylacetone and ethyl butyl ketone.

Diphenylacetylene (tolane), under similar conditions, yields deoxybenzoïn, which can be separated from the unaltered tolane by means of alcohol.

It is finally shown that the above hydrocarbons contained no trace of hydrogen chloride, which might act as a condensing agent, and, therefore, the general reaction given above shows a direct synthesis of ketones from the unsaturated hydrocarbons of the acetylene series. J. J. S.

**Compounds of Mercuric Cyanide with Metallic Chlorides.** By RAOUL VARET (*Compt. rend.*, 1895, **121**, 348—351).—Experiments were made with the view of ascertaining whether compounds of the type $2Hg(CN)_2,M''Cl_2 + nH_2O$ have really this constitution, or are compounds of a double cyanide and mercuric chloride,

$$Hg(CN)_2,M''(CN)_2,HgCl_2.$$

The first column contains the heat of dissolution of the crystallised salt; the second column the heat developed by mixing dilute solutions of mercuric cyanide and the metallic chloride; the third column the heat of formation of the solid double salt from solid mercuric cyanide, the solid metallic chloride and liquid water.

| | I. | II. | III. |
|---|---|---|---|
| $2Hg(CN)_2,2NaCl + 2\frac{1}{2}H_2O$ ....... | −16·20 Cal. | +0·33 Cal. | + 7·95 Cal. |
| $2Hg(CN)_2,2NH_4Cl + 1\frac{1}{2}H_2O$ ...... | −14·80 ,, | +0·38 ,, | + 1·18 ,, |
| $2Hg(CN)_2,BaCl_2 + 5H_2O$ ......... | −17·1 ,, | +0·45 ,, | +13·55 ,, |
| $2Hg(CN)_2,SrCl_2 + 6H_2O$ ......... | −15·80 ,, | +0·45 ,, | +21·25 ,, |
| $2Hg(CN)_2,CaCl_2 + 6H_2O$ ......... | −14·20 ,, | +0·50 ,, | +26·1 ,, |
| $2Hg(CN)_2,MgCl_2 + 6H_2O$......... | − 9·9 ,, | +0·50 ,, | +40·4 ,, |
| $2Hg(CN)_2,ZnCl_2 + 7H_2O$......... | −13·30 ,, | +0·90 ,, | +23·8 ,, |
| $Hg(CN)_2,CdCl_2 + 2H_2O$......... | − 9·30 ,, | +0·38 ,, | + 6·48 ,, |

These results indicate that the whole of the cyanogen remains in direct combination with the mercury, and this view is supported by the fact that the cold solutions of the double salts are not alkaline to litmus, and, if heated at 30° with a soluble picrate, no isopurpurate is formed. If, however, the solutions are boiled, they become slightly alkaline, and give the isopurpurate reaction, from which it follows that, at the higher temperature, there is a migration of atoms, and part of the cyanogen becomes combined with the alkali or alkaline-earth metal. C. H. B.

**Copper Ferrocyanide.** By GUSTAV RAUTER (*Zeit. angw. Chem.*, 1895, 315—316).—This is an investigation of the nature of the precipitate formed, under varying conditions, by the interaction of copper sulphate and potassium ferrocyanide.

The upshot is that the precipitate always retains potassium ferrocyanide, but that this must not be looked on as a chemical constituent but only as an impurity. Owing to the great difficulty experienced in completely washing the voluminous deposit, a certain amount of potash is obstinately retained. L. DE K.

**Sulphur as a Preservative of Chloroform.** By L. ALLAIN (*J. Pharm.*, 1895, [6], **2**, 252—255).—Chloroform, saturated with sulphur in the cold, may be kept in direct sunlight for months, without undergoing change; in particular, no carbonyl chloride is formed. This stability is not due to any change produced by the sulphur, for the redistilled liquid rapidly decomposes when exposed to the same conditions. As the anæsthetic properties of the chloroform are not modified by the presence of the sulphur, the addition of this preservative is to be recommended. JN. W.

**Nitro-alcohols.** By LOUIS HENRY (*Compt. rend.*, 1895. **121**, 210—213).—Nitromethane and formaldehyde, in presence of a small quantity of potassium carbonate, react quantitatively with production of *tertiary nitrotrihydroxybutane*, $NO_2 \cdot C(CH_2 \cdot OH)_3$, a white, solid compound, which crystallises in needles or in large prisms melting at 158—159°, and soluble in water, alcohols, and acetone, but less soluble in ether. Attempts to obtain products of the interaction of one molecule of nitromethane and one and two molecules respectively of formaldehyde were unsuccessful.

Nitroethane and formaldehyde, in presence of potassium carbonate, yield the compound $NO_2 \cdot CMe(CH_2 \cdot OH)_2$, which is *tertiary nitrodihydroxybutane* or tertiary *nitroisobutylenic glycol.* It crystallises very readily, melts at 139—140°, and is soluble in water, alcohols, and acetone, but less soluble in ether. Secondary nitropropane and formaldehyde, under similar conditions, yield the nitroisobutylic alcohol, $NO_2 \cdot CMe_2 \cdot CH_2 \cdot OH$, which melts at 82°, crystallises very readily, is very soluble in alcohols and acetone, but less soluble in water, and more soluble in ether than the two preceding compounds.

From these results it follows that the reaction capacities of the three nitroparaffins with respect to formaldehyde are proportional to the number of hydrogen atoms attached to the group $C \cdot NO_2$, and there is little doubt that tertiary nitrobutane, $NO_2 \cdot CMe_3$, would have no action on formaldehyde or the other aldehydes of the same series. C. H. B.

**Glucoseacetone.** By EMIL FISCHER (*Ber.*, 1895, **28**, 2496—2497). —The author has previously shown (Abstr., 1895, i, 440) that *d*-glucose, arabinose, and fructose react with two molecules of acetone, and rhamnose with only one; it is now shown that glucose can also form a condensation product with one molecule of acetone. This substance has the composition $C_6H_{10}O_6\colon CMe_2$, and the author terms it *glucose-acetone.* It differs from the alcoholic glucosides in the fact that it is not acted on by emulsin or by the enzyme of yeast; it forms small, felted needles, melts at 160—161° (corr.), is soluble in water, and is lævorotatory. It has a bitter taste, does not sublime at 100°, but may be distilled in small quantities without undergoing decomposition; it is readily decomposed by dilute acids, but has no action on Fehling's solution. J. J. S.

**Inversion of Maltose and Isomaltose by means of Yeast.** By CARL J. LINTNER (*Chem. Centr.*, 1895, i, 271—272; from *Zeit. Ges. Brauw.*, **17**, 414—415).—Referring to the investigations of E. Fischer on the influence of the configuration of the molecule on the action of enzymes, the author has observed that the hydrolysis of maltose proceeds most rapidly with yeast powder, the aqueous extract is less active, and precipitated invertin least. Isomaltose is more readily attacked than maltose. The enzyme is less soluble than invertin, and appears to be more closely allied to the glycolytic ferments. The presence of dextrose in small quantity in Munich lager beer, is due to the action of yeast on isomaltose. J. B. T.

**The Inulin of Garlic, Hyacinth, Narcissus, and Tuberose.** By R. Chevastelon (*J. Pharm.*, 1895, [6], **2**, 83—86; from *Inaug. Diss.*, *Paris*, 1894).—The reserve material of the bulbs and other underground parts of certain monocotyledons is a kind of inulin. To separate this substance, the bulbs, &c., are cut into small fragments, and digested with ether, to cause the expulsion of the sap from the cells; the sap collecting at the bottom of the vessel, together with a further amount remaining in the fragments, and liberated by pressure, is purified with basic lead acetate and animal charcoal, and the inulin precipitated by baryta water. The insoluble baryta compound of the carbohydrate is decomposed by carbonic anhydride, and the inulin precipitated with alcohol-ether as a syrup. Finally, this is dried in succession by washing with alcohol and ether, and then under diminished pressure, and at 100°.

The *inulin of garlic*, $C_6H_{10}O_5$, is a white, inodorous, amorphous powder, distinct from the inulin of the Jerusalem artichoke. Its taste is insipid, and it is very deliquescent. It melts at 175—176°, and is soluble in water and dilute alcohol, but only sparingly in strong alcohol. The rotatory power is $[\alpha]_D = -39°$.

It does not reduce alkaline copper tartrate, and is completely hydrolysed by acids to levulose. It is precipitated neither by normal nor by basic lead acetate, except in presence af ammonia. It is not hydrolysed by amylase (malt diastase), but is resolved into levulose by an enzyme *inulase*, which is secreted by *Aspergillus niger*, and is similar to the enzyme of the inulin of the Jerusalem artichoke, and of *Atractylis*. The inulin of garlic is not fermented either by hydrolytic or non-hydrolytic yeasts.

The sap from the offshoots of the garlic bulbs contains only traces of reducing sugars, and yields nothing but levulose on hydrolysis, so that it contains no reserve material but inulin.

The inulin of the sap of the bulbs of various species of hyacinth is identical with that from garlic. The bulbs also contain a small amount of levulose, and a large amount of starch, so that here the reserve material is stored in both soluble and insoluble forms.

The inulin from the bulbs of the narcissus and tuberose is also identical with that from garlic; neither of these contains starch, but the narcissus sap contains both glucose and levulose, whilst that of the tuberose contains glucose only.

Various other bulbous monocotyledons were examined, such as the onion, tulip, and iris. Jn. W.

**Glyoxylic acid and its Behaviour towards Carbohydrates.** By Carl Boettinger (*Arch. Pharm.*, 1895, **233**, 287—294).—Glyoxylic acid acts as a hydrolysing agent towards starch and cane sugar, and it prevents the fermentation of the products formed, for it acts on yeast as a poison. From glyoxylic acid and glucose, a syrup is obtained, which is asserted to have the constant composition

$C_6H_{12}O_6,C_2H_2O_3 + H_2O$; with galactose a similar compound *may* have been obtained, and with levulose a compound $C_6H_{12}O_6.2C_2H_3O_2$.

C. F. B.

**Preparation of Glycogen.** By D. HUIZINGA (*Pflüger's Archiv*, 1895, **61**, 32—38).—On account of the opalescence of glycogen solutions, the presence of albumoses in small quantity can only be ascertained by means of the biuret reaction or by Millon's reagent; with the former, not less than 0·5 per cent. can be detected; with the latter, a distinct orange colour is obtained when the solution contains 0·1 per cent.; if the albumose is precipitated by means of a solution containing sodium tungstate (100 parts), phosphoric acid (50 parts), concentrated hydrochloric acid (10 parts), and water (500 parts), and the dried precipitate treated with Millon's reagent, the presence of 0·02 per cent. of albumose may be distinctly recognised. The above experiments were made with albumose prepared from egg albumin; the presence of glycogen is without effect on the reactions. The boiling water usually employed for the preparation of glycogen extracts albumoses in considerable quantity, and their subsequent separation is attended with considerable difficulty; trichloracetic acid, which Fränkel used instead of water, also dissolves albumoses, as do sulphosalicylic acid and formaldehyde solutions; saturated solution of mercuric chloride extracts pure glycogen, but the resulting liquid is often unsuitable for filtration; the best results were obtained by the use of equal parts of saturated solution of mercuric chloride and Esbach's reagent, made by dissolving picric acid (10 grams) and citric acid (20 grams) in water (1 litre). The glycogen, after washing with alcohol and ether-alcohol, was free from albumoses, and contained 0·62—0·80 per cent. of ash. This method, although good for the preparation of glycogen, is not adapted for its quantitative estimation, as it yielded only 78—89 per cent. of the total glycogen determined by Külz's method.

J. B. T.

**Oxycellulose.** By R. W. TROMP DE HAAS and BERNHARD TOLLENS (*Annalen*, 1895, **286**, 296—300; compare Abstr., 1893, i, 295).—The authors have hydrolysed, with sulphuric acid, oxycellulose obtained by treating fir saw-dust with nitric acid. Twenty grams of oxycellulose was added slowly to 100 grams of concentrated sulphuric acid mixed with 20 grams of water, 80 grams of water being added after an hour; on the following morning, 2·5 litres of water were added to the liquid, which was heated in a reflux apparatus for five hours in boiling water. After neutralising the pale yellow liquid with calcium carbonate, the filtered solution yielded 3 grams of dextrose, having the specific rotatory power $[\alpha]_D = +51·2°$. Determination of cellulose by Lange's method indicated the presence of about 20 per cent., whilst 3 per cent. of furfuraldehyde was obtained from the oxycellulose by distillation with hydrochloric acid.

From these results, the authors conclude that the oxycellulose obtained from fir-wood is not identical with the oxycelluloses investigated by Cross and Bevan, Witz, and Nastjukoff.

M. O. F.

**Remarks on the Foregoing Paper.** By Bernhard Tollens (*Annalen*, 1895, **286**, 301—302).—Many substances which yield furfuraldehyde when distilled with hydrochloric acid are found to contain, in some form, pentoses or glycuronic acid. This is not the case with the oxycellulose described in the foregoing abstract, and the author suggests glycoson, $C_6H_{10}O_6$, as a possible source of the production of furfuraldehyde from this substance. M. O. F.

**Constitution of Pectin Substances.** By Bernhard Tollens (*Annalen*, **286**, 292—295).—From a consideration of the properties of these substances and the products of their hydrolysis, the author regards them as carbohydrates combined chemically with acids, this view having been already advanced by O'Sullivan regarding the vegetable gums. M. O. F.

**Pectin Substances.** By R. W. Tromp de Haas and Bernhard Tollens (*Annalen*, 1895, **286**, 278—292).—Many attempts have been made to establish a relationship between pectins and vegetable gums (carbohydrates). Accurate determinations of composition are essential to generalisations of this character, and the authors have accordingly prepared and analysed pectin substances from various sources, the proportion between hydrogen and oxygen being indicated in each case. The pectins were precipitated by alcohol in the juice expressed from the fruits, and, after being washed with ether, were dried over sulphuric acid.

The analytical results are embodied in the following table.

| Pectin. | Percentage of C. | Ratio of H to O. | Percentage of Ash. |
|---|---|---|---|
| Apple A | 43·35 | 1 : 7·9 | 5·95 |
| Apple B | 43·46 | 1 : 7·4 | 6·54 |
| Cherry | 42·42 | 1 : 7·7 | 20·50 |
| Rhubarb A | 43·31 | 1 : 7·3 | 4·19 |
| Rhubarb B | 42·89 | 1 : 8·9 | 6·88 |
| Currant | 46·87 | 1 : 8·5 | 5·02 |
| Plum | 42·92 | 1 : 8·5 | 3·34 |
| Swede A | 41·08 | 1 : 9·0 | 7·29 |
| Swede B | 42·33 | 1 : 8·8 | 1·97 |

From this it is clear that the pectins are allied in composition to the carbohydrates, and that the low proportion of hydrogen to oxygen (1 : 10—12) recorded by previous observers is not confirmed.

Hydrolysis of these pectins leads to the formation of hexoses or pentoses. M. O. F.

**Preparation of Methylamine.** By André Brochet and R. Cambier (*J. Pharm.*, 1895, [6], **2**, 172—173; from *Rev. Chim. Industr.*, June, 1895; compare Abstr., 1895, i, 642).—Formaldehyde (20 kilos. of 40 per cent.) is distilled with ammonium chloride (10 kilos.). The action commences at 40°, when methylal passes over, and the distillate up to 95° contains 60—79 per cent. of that substance. The residue is evaporated down until ammonium chloride commences to crystallise out, and, on cooling, the whole excess of that substance separates. The liquid remaining is a nearly pure solution of methylamine hydrochloride, from which the pure substance is obtained by evaporation under low pressure and recrystallisation from alcohol. The yield of 95 per cent. methylamine hydrochloride, melting at 210°, is 8·5 kilos. with the above quantities, and, at the same time, 3·8 kilos. of methylal and 2·2 kilos. of carbonic anhydride are formed, and 3·5 kilos. of ammonium chloride recovered unchanged. JN. W.

**Chloro-derivatives of Amines.** By ARMAND BERG (*Ann. Chim. Phys.*, 1895, [7], **3**, 289—361).—The normal butylamines have been prepared according to Hofmann's method by the action of butylic chloride on a dilute alcoholic solution of ammonia. The bases are first separated by means of their hydrochlorides, and then the primary base is purified by conversion into *dibutyloxamide*, $C_2O_2(NHC_4H_9)_2$, which melts at 153°, and is but sparingly soluble in water. The mother liquor contains *butylamine butyloxamate*, $C_4H_9{\cdot}NH{\cdot}CO{\cdot}COO{\cdot}NH_3{\cdot}C_4H_9$, which, when heated in aqueous solution with calcium chloride, yields *calcium butyloxamate*,

$$(C_4H_9{\cdot}NH{\cdot}CO{\cdot}COO)_2Ca + 2H_2O.$$

*Butylamine oxalate*, $C_2O_2(ONH_3{\cdot}C_4H_9)_2$, is deposited on evaporating the mother liquid of the oxamate.

*Dibutylamine hydrochloride* is made use of in the separation of the secondary base. The *aurochloride*, $NH_2(C_4H_9)_2AuCl_4$, is precipitated when concentrated solutions of gold chloride and dibutylamine hydrochloride are mixed; it crystallises in long, golden needles, and melts at 170°. The *stannichloride*, $2NH_2(C_4H_9)_2Cl,SnCl_4 + H_2O$, crystallises in long, colourless needles. Dibutylamine hydrogen oxalate, $COOH{\cdot}COO{\cdot}NH_2(C_4H_9)_2$, is much more readily soluble in water than the corresponding diisobutylamine salt. *Dibutylamine picrate* melts at 59·5°.

The tributylamine hydrochloride is extremely deliquescent. The *picrate* melts at 100·5°, and is very sparingly soluble in water.

The isobutylamines have been prepared by a similar method; the author finds that when a mixture of isobutylic chloride (1 mol.) and aqueous ammonia (1 mol.), to which just sufficient alcohol for solution has been added, is heated at 110—115°, the primary base is the chief product. It may be purified by conversion into the oxamide (Malbot, Abstr., 1891, 817). The pure base boils at 67·9—68°. (Reimer gives 62—65°, and Perkin 68—69°.) The secondary and tertiary bases are best separated by conversion into the acid oxalates. Diisobutylamine boils at 140·6—140·8°. (Reimer gives 122—125°, Malbot 137°, and Perkin 139—140°.)

The amylamines have been prepared and separated by similar methods. *Amylamine amyloxamate*, $C_5H_{11}{\cdot}NH{\cdot}CO{\cdot}COO{\cdot}NH_3{\cdot}C_5H_{11} + H_2O$, crystallises in colourless needles, and is readily soluble in hot water. *Calcium amyloxamate*, $(C_5H_{11}{\cdot}NH{\cdot}CO{\cdot}COO)_2Ca + H_2O$, is sparingly soluble in cold water, readily in boiling, and crystallises in slender, colourless needles.

Most of the chloramines have been described before (Abstr., 1890, 952; 1892, 804 and 1172; 1893, i, 296 and 497). The monochloramines were prepared by the action of a concentrated solution of sodium hypochlorite on an aqueous solution of the hydrochloride of the amine. The dichloramines were prepared by Tcherniak's method.

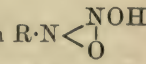
*Butylchloramine*, $C_4H_9{\cdot}NHCl$, is a faintly yellowish oil, has a sharp odour, is insoluble in water, decomposes on heating, and has a sp. gr. of 0·992 at 0°. *Butyldichloramine*, $C_4H_9{\cdot}NCl_2$, is a yellow liquid, with a sp. gr. = 1·112 at 0°. It boils at 71° under a pressure of 80 mm. *Dibutylchloramine*, $(C_4H_9)_2NCl$, is an oily liquid with a sp. gr. of 0·906 at 0°, and boils at 99° under a pressure of 52 mm.; it slowly decomposes when kept. These chloramines undergo decompositions similar to those given for the chloramines which have been previously described; thus when acted on by reducing agents they are converted into the hydrochlorides of the corresponding bases. Quinol, pyrogallol, and gallic acid give colorations with the chloramines. Sulphuric acid acts on the monochloramines, converting them into the base and the corresponding dichloramines. Amylchloramine and silver nitrite act in the presence of alcohol, forming the silver derivative of amylnitramine, which crystallises in fine tablets.

The reactions with potassium iodide and potassium cyanide are similar to those previously described. J. J. S.

**Constitution of the Isonitramines.** By Wilhelm Traube (*Ber.*, 1895, **28**, 2297—2302; compare Abstr., 1895, i, 592).—The isonitraminic acids are converted, by boiling with dilute hydrochloric acid, into the corresponding amidoxylic acids, which may be reconverted into the isonitraminic acids by the action of nitrous acid. *Hydroxylamidoacetic acid*, $HO{\cdot}NH{\cdot}CH_2{\cdot}COOH$, crystallises in lustrous, rhombic tablets melting at 135°, and reduces Fehling's solution at the ordinary temperature. *Hydroxylamidophenylpropionic acid*,

$$CH_2{\cdot}Ph{\cdot}CH(NH{\cdot}OH){\cdot}COOH,$$

crystallises in prisms melting at 157—158°. When this acid is treated with nitrous acid, it yields isonitraminephenylpropionic acid, identical with that prepared from ethylic benzylacetoacetate and nitric oxide, along with another substance which has the formula $C_8H_8NO$. This second compound does not reduce Fehling's solution, and explodes when heated.

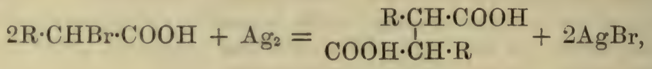
The isonitraminic acids probably have the constitution  $R{\cdot}N\Big\langle\begin{array}{l}NOH\\ \;|\\ O\end{array}$, since they are formed by the action of nitrous acid on the amidoxylic acids. A. H.

**Existence of Imido-ethers derived from Hydrocyanic acid.** By Adolf Pinner (*Ber.*, 1895, **28**, 2454—2458).—A reply to the criticisms of J. U. Nef (*Annalen*, 1895, **287**, 328). Nef has stated that the substance, previously described by the author as the hydrochloride of the ethylic ether of formimide, $NH{:}CH{\cdot}OEt,HCl$, is a mixture of five different compounds. In this paper reasons are given why it should still be considered a homogeneous substance. J. J. S.

**Condensation of Isovaleraldehyde.** By L. Kohn (*Compt. rend.*, 1895, **121**, 259—260).—Isovaleraldehyde and potassium hydroxide do not yield secondary glycols analogous to those obtained by Fossek from isobutaldehyde, but two products are formed. One boils at 82° under a pressure of 15 mm., or 187° under 746 mm., and oxidises very easily with formation of an acid, $C_{10}H_{18}O_2$. The other boils at 140° under a pressure of 18 mm., and seems to be a polymeride of valeral.
C. H. B.

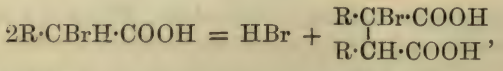
**Action of finely divided Silver on Halogen Derivatives of Aliphatic acids.** By Carl Hell (*Ber.*, 1895, **28**, 2439—2445; compare J. Wislicenus, *Annalen*, **149**, 215; Hell, *Ber.*, **6**, 28; **7**, 319; **10**, 2229; **13**, 473; **22**, 48).—The author considers that the general equations previously given by him to represent the action of finely divided silver on the halogen derivatives of the fatty acids do not account for the formation of many of the compounds obtained in the reaction. It is now suggested that in the formation of dicarboxylic acids from α-halogen (*e.g.* bromine) derivatives of the fatty acids, two reactions occur: (1) the bromine atoms are removed by the silver, and the two residues then unite to form a dicarboxylic acid; (2) hydrogen bromide is removed by the union of the bromine of 1 mol. with a hydrogen atom in the α-position to the bromine of a second molecule.

The author considers that this accounts for the formation of tetramethylsuccinic and trimethylglutaric acids from bromisobutyric acid, and that it also accounts for the formation of both stereoisomeric dialkylsuccinic acids by similar methods. Thus by reaction (1) we obtain one modification,

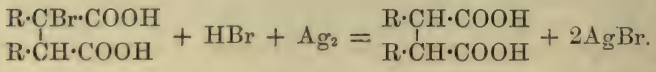


$$2R{\cdot}CHBr{\cdot}COOH + Ag_2 = \begin{array}{c}R{\cdot}CH{\cdot}COOH\\ |\\ COOH{\cdot}CH{\cdot}R\end{array} + 2AgBr,$$

and by reaction (2) we obtain the second modification—



$$2R{\cdot}CBrH{\cdot}COOH = HBr + \begin{array}{l}R{\cdot}CBr{\cdot}COOH\\ \;\;|\\ R{\cdot}CH{\cdot}COOH\end{array},$$



$$\begin{array}{l}R{\cdot}CBr{\cdot}COOH\\ \;\;|\\ R{\cdot}CH{\cdot}COOH\end{array} + HBr + Ag_2 = \begin{array}{l}R{\cdot}CH{\cdot}COOH\\ \;\;|\\ R{\cdot}CH{\cdot}COOH\end{array} + 2AgBr.$$

A third reaction, which often occurs simultaneously, is the removal of hydrogen bromide from 1 mol., and the formation of an unsaturated acid of the acrylic series. The formation of pyrocinchonic acid from α-bromopropionic acid and silver is probably due to a similar reaction.
J. J. S.

**Electrolytic Synthesis of Monocarboxylic acids of the Fatty Series.** By Wilhelm von Miller and Hans Hofer (*Ber.*, 1895, **28**, 2427—2439; compare Abstr., 1894, i, 228).—The authors have made electrolytic experiments with mixtures of potassium acetate and potassium ethylic succinate in Hofer's apparatus (*Ber.*, **27**, 464).

They show that when a solution of potassium ethylic succinate is used as the positive electrolyte, and a concentrated solution of potassium carbonate (kept neutral by passing in carbonic anhydride) as the negative, theoretical yields of ethylic adipate may be obtained; whereas Crum-Brown and Walker by their method obtained a yield of only 35 per cent. (Abstr., 1891, 1192; 1893, i, 394). If a mixture of potassium acetate and potassium ethylic succinate is used as the positive electrolyte, and the negative is the same as in the previous case, a yield of 40—69 per cent. of ethylic butyrate can be obtained. A small quantity of the adipate is formed at the same time, this amount varying with the composition of the original mixture used.

By replacing the potassium acetate by potassium propionate, butyrate, and isobutyrate respectively, the authors have succeeded in synthesising ethylic valerate, caproate, and isobutylacetate.

The gases evolved during the electrolysis were examined in each case. They contain carbonic anhydride (73—82 per cent.), oxygen (0·3—0·4 per cent.), carbonic oxide (1—3 per cent.).

It has also been found possible to obtain ethylic iodide, together with iodoform and sodium iodate, by the electrolysis of a solution containing sodium propionate as the positive electrolyte and potassium iodide as the negative. With potassium succinate as the positive, *β*-iodopropionic acid is obtained. When sodium propionate and potassium nitrite were used as the two electrolytes, a small quantity of nitroethane was obtained; and when potassium acetate and potassium glycollate were used, the authors obtained formaldehyde at the negative pole and ethylic alcohol at the positive.

Similar experiments with a mixture of potassium ethylic malonate and potassium acetate at the positive pole, and potassium carbonate at the negative, gave ethylic propionate as the chief product; but with a mixture of potassium ethylic malonate and potassium propionate at the positive pole, ethylic valerate was formed, and similarly with a mixture of the malonate and potassium butyrate, ethylic valerate was the chief product. J. J. S.

**β-Hydroxy-α-dimethylisocaproic acid and Diisopropylglycollic acid.** By ALEXANDER BARYLOWITSCH (*Ber.*, 1895, **28**, 2463—2466).—Reformatsky has obtained *β-hydroxy-α-dimethylisocaproic acid*, $CHMe_2{\cdot}CH(OH){\cdot}CMe_2{\cdot}COOH$, by the action of zinc and ethylic bromisobutyrate on isobutaldehyde. This acid melts at 92°, whereas the acid described by Wohlbrück and Hantzsch under the same name melts at 111—112°. The author has further investigated the acid of Wohlbrück-Hantzsch (Abstr., 1887, 1099), and finds that it is not *β*-hydroxy-*α*-dimethylisocaproic acid, but is identical with the diisopropylglycollic acid, $OH{\cdot}C(CHMe_2)_2{\cdot}COOH$, previously described by Markovnikoff. J. J. S.

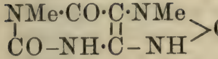
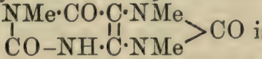
**Glucic acid** (?). By HEINRICH WINTER (*Chem. Centr.*, 1895, i, 371—372; from *Z. Ver. Rübenzuck*, 1894, 1049—1051).—Invert sugar solution (1 per cent.), heated with lime water (0·5 per cent.) at 66·5°, gives a white, voluminous, flocculent precipitate which probably consists of basic calcium glucate; it dissolves when further heated, becomes dark brown on exposure to air, and is sparingly soluble in water. The precipitate cannot be removed by filtration; it was washed six times with lime water by decantation, treated with dilute sulphuric acid, and extracted with ether; this extract, when evaporated, left a syrup, together with needle-shaped crystals, probably consisting of glucic acid; after remaining for some time in a desiccator, the needles disappeared, and crystals resembling those of cane sugar were produced (apoglucic acid?); finally, these dissolved, the syrup darkened, gas was evolved, and a black resin was formed which yielded carbonic anhydride and formic acid when distilled with steam. The acid could not be recrystallised.

J. B. T.

**New Synthesis of Uric acid and of its Methyl Derivatives.** By Emil Fischer and Lorenz Ach (*Ber.*, 1895, **28**, 2473—2480; compare Liebig and Wöhler, *Annalen*, **24**, 284; Schlieper and Baeyer, *Annalen*, **127**, 3; Horbaczewski, Abstr., 1885, 1050; 1887, 918; Behrend and Roosen, Abstr., 1887, 581).—When Schlieper and Baeyer's pseudo-uric acid is fused with a large excess of oxalic acid at a temperature of 145—185° for 10 minutes, it loses a molecule of water, and yields uric acid. The dimethylpseudouric acid of Techow (Abstr., 1895, i, 84), when treated in a similar manner, yields a dimethyluric acid, which melts at 370°; it is moderately soluble in hot water, sparingly in cold water, in alcohol, and in acetone, but readily dissolves in ammonia, forming an *ammonium salt*, which can be obtained in a crystalline form by concentrating the solution. The *silver salt* is a gelatinous precipitate, which decomposes slowly at ordinary temperatures, but much more readily when warmed.

Another compound, which is formed in small quantity by the action of oxalic acid on dimethylpseudouric acid is E. Fischer and Reese's deoxyamalic acid (Abstr., 1884, 466); this forms a sparingly soluble sodium salt, and readily yields murexoïn when treated with bromine and then with ammonia. If dimethylpseudouric acid is added to a mixture of acetic anhydride and zinc chloride, a yield of 25 per cent. of $\gamma$-dimethyluric acid is obtained. When the lead salt of this acid is heated, at 120°, with methylic iodide and ether, a new *$\beta$-trimethyluric acid* is formed. This $\beta$-acid melts between 315° and 320°, at the same time undergoing decomposition; it is readily soluble in dilute alkalis, moderately in hot alcohol, and only sparingly in cold water and in alcohol. It gives the murexide reaction, is not readily acted on by phosphorus pentachloride, and, when heated with concentrated hydrochloric acid at 150°, yields carbonic anhydride, methylamine, and glycocine. When the lead salt of $\beta$-trimethyluric acid is further methylated, it yields the same tetramethyluric acid as is obtained from the $\alpha$-trimethyl acid.

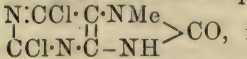
J. J. S.

**Formation of Methyluric Acids from Theobromine.** By Emil Fischer (*Ber.*, 1895, **28**, 2480—2495).—When bromotheobromine is heated with normal potassium hydroxide solution for eight hours on the water bath, the chief product is *δ-dimethyluric acid*,  $\begin{matrix}\mathrm{NMe{\cdot}CO{\cdot}C{\cdot}NMe}\\ \mathrm{CO{-}NH{\cdot}C{-}NH}\end{matrix}\!>\!\mathrm{CO}$, accompanied by a small quantity of a bromine derivative, which can be removed by reduction with hydriodic acid. The acid is decomposed at a higher temperature, when it evolves unpleasant smelling gases; it is only sparingly soluble in cold water, and crystallises from boiling water in prismatic plates, and readily gives the murexide reaction. The *ammonium*, *sodium*, and *potassium salts* are readily soluble in water, the *silver salt* forms a colourless, amorphous powder soluble in ammonia. When the lead salt is treated with methylic iodide and ether at 165—170°, it yields the trimethyluric acid previously described by the author (Abstr., 1884, 1309), to which the formula  $\begin{matrix}\mathrm{NMe{\cdot}CO{\cdot}C{\cdot}NMe}\\ \mathrm{CO{-}NH{\cdot}C{\cdot}NMe}\end{matrix}\!>\!\mathrm{CO}$ is given.

Chlorocaffeïne, when heated with alcoholic potash, readily yields ethoxycaffeïne; aqueous potash reacts in a more complicated manner, and even with very dilute alkali only a small quantity of hydroxycaffeïne is formed. Bromoxanthine is very stable, and the greater part remains unaltered, even when heated for six hours at 135—140° with normal potassium hydroxide.

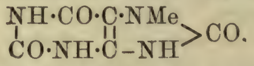
*Chlorodioxydimethylpurin*, $C_7H_7N_4O_2Cl$, is obtained when δ-dimethyluric acid (1·5 parts) is heated with phosphorus pentachloride (2 parts) and oxychloride (4 parts) at 140—145°. It forms small, colourless needles, and melts at 290° (corr.), at the same time undergoing decomposition. When reduced with hydriodic acid and phosphonium iodide, it gives *β-dioxydimethylpurin*, which is entirely decomposed at 370°; this is readily soluble in dilute alkalis and mineral acids, gives an amorphous silver salt, an *aurochloride* which crystallises in fine, yellow needles, and also a yellow *platinochloride*. The base, in contradistinction to the xanthine bases, does not give the murexide reaction.

*β-Trichloromethylpurin*, is the final product of the action of phosphorus pentachloride on δ-dimethyluric acid, on theobromine or on caffeïne, the yield is much better when chlordioxydimethylpurin is first formed, and this is then treated with an excess of phosphorus pentachloride. It is readily soluble in hot alcohol and in benzene, sparingly in hot water, crystallises in fine, colourless needles, melts at 159—161° (corr.), and may be distilled in small quantities.

*β-Dichloroxymethylpurin*,  $\begin{matrix}\mathrm{N{:}CCl{\cdot}C{\cdot}NMe}\\ \mathrm{CCl{\cdot}N{\cdot}C{-}NH}\end{matrix}\!>\!\mathrm{CO}$, is formed when β-trichloromethylpurin is boiled with 40 times its weight of 20 per cent. hydrochloric acid for 10—15 minutes. It crystallises in small, colourless needles, melts and evolves gas at 278° (corr.), and is readily soluble in hot acetone but only sparingly in chloroform. It has acid properties, readily dissolves in cold alkalis, and yields a *silver derivative* which crystallises in slender needles; when the silver or lead salt is methylated, it yields dichloroxydimethylpurin (Abstr., 1884, 996).

*β-Oxymethylpurin*, $C_6H_6N_4O$, is obtained by the reduction of β-dichloroxymethylpurin with hydriodic acid and phosphonium iodide; it crystallises in fine, colourless needles, melts at 266—267° (corr.), and is readily soluble in hot water, but only sparingly in cold. It forms salts with both acids and alkalis, the *platinochloride* forms large, yellow crystals, and the *aurochloride*, $C_6H_6N_4O,HAuCl_4$, large, yellow plates.

When heated at 130° with hydrochloric acid (sp. gr. 1·19), trichloromethylpurin is converted into *γ-methyluric acid*,



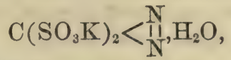
$$\left.\begin{array}{l} NH\cdot CO\cdot C\cdot NMe \\ \,|\qquad\qquad\; \| \\ CO\cdot NH\cdot C-NH \end{array}\right> CO.$$

This acid crystallises with $1H_2O$, which it loses at 140°, decomposes at 370—380° without melting, and readily gives the murexide test. The *sodium* and *ammonium salts* are readily soluble in water, the *silver salt* is obtained quite colourless on the addition of a small quantity of silver nitrate to a solution of the ammonium salt; if too much silver nitrate is used, the salt becomes black. When heated with fuming hydrochloric acid at 170°, it is decomposed into carbonic anhydride, ammonia, and sarcosine; and when oxidised with potassium chlorate and hydrochloric acid, it yields alloxan and monomethylurea.

When trimethyluric acid is treated with phosphorus pentachloride and oxychloride at 130—150°, the dichloroxydimethylpurin previously described is formed. J. J. S.

**Action of Sulphurous Acid on Potassium Cyanide: Diazomethanedisulphonic acid.** By HANS VON PECHMANN and PHILIPP MANCK (*Ber.*, 1895, **28**, 2374—2383; compare *ibid.*, Ref., 522).—*Hydrogen potassium amidomethanedisulphonate*, $HSO_3\cdot CH(NH_2)\cdot SO_3K$, is obtained by dissolving 100 grams of 99 per cent. potassium cyanide in a solution of hydrogen potassium sulphite, prepared by saturating a solution of 150 grams of caustic potash in 600 grams of water with sulphurous anhydride; the acid liquid is heated on the water bath, and becomes alkaline after 30—40 minutes. The solution is then carefully acidified with hydrochloric acid, and again warmed, addition of acid being repeated until the acidity is permanent, this being usually the case after 1½—2 hours. On adding concentrated hydrochloric acid to the cold liquid, about 200—250 grams of the hydrogen potassium salt crystallises out. It is a snowy powder, which dissolves but sparingly in water, yielding an acid solution; boiling water resolves it into the components.

*Dipotassium amidomethanedisulphonate* is prepared by allowing the mixed solution of potassium cyanide and hydrogen potassium sulphite to remain for several days at the ordinary temperature without previous treatment with acid; it crystallises from the liquid in rhombohedra, or in nodules of slender needles. It is more conveniently prepared by neutralising a solution of the foregoing salt with potassium carbonate. Recrystallised from hot water rendered feebly alkaline, it contains $1H_2O$, which is removed at 105°; it dissolves very readily in water, undergoing decomposition when the solution is boiled, yielding the components. Formic acid, ammonia, potassium thiosulphate, and potassium thiocyanate are also produced, the two last-named being secondary products due to the action of potassium sulphite on formic acid and of potassium thiosulphate on potassium cyanide respectively.

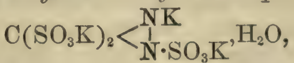


*Dipotassium diazomethanedisulphonate*, $\mathrm{C(SO_3K)_2}{<}\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}\mathrm{,H_2O}$, is prepared in the following manner. Hydrogen potassium amidomethanedisulphonate (23 grams) is mixed with water (34 grams) and treated with a 66 per cent. solution of potassium nitrite (15 grams) at 15—16°; as the salt passes into solution, the temperature gradually rises to 40—45°, and, after 10—15 minutes, the orange-yellow liquid, which effervesces slightly, is rendered alkaline with caustic potash, and allowed to cool. The salt, recrystallised from 2 parts of boiling water containing a small quantity of potash, is obtained in orange-yellow needles or prisms containing $1H_2O$, which is removed in a vacuum at 60—90°. At higher temperatures, water and sulphurous anhydride are liberated, the salt becoming colourless; in dealing with a small quantity, this change occurs at 210°, and the residue consists of potassium sulphate, thiosulphate, and formate. The salt is readily soluble in water, forming a neutral solution which gradually becomes acid and evolves gas, energetic liberation of nitrogen taking place in the boiling liquid; this gas is evolved quantitatively on treating the salt with acids.

*Dipotassium iodomethanedisulphonate*, $\mathrm{CHI(SO_3K)_2,2H_2O}$, is prepared by adding 30 per cent. hydriodic acid (12 grams) to a solution of the diazo-salt (10 grams) in water (100 grams); after 10 hours, the solution is treated with alcohol, and the precipitate thus obtained redissolved in a small quantity of warm water to which acetone is then added, the salt being obtained in aggregates of long needles. It contains $2H_2O$ which is eliminated at 105°; the boiling solution yields silver iodide when treated with silver nitrate.

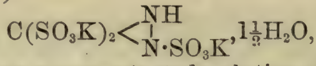
*Dipotassium diodomethanedisulphonate*, $\mathrm{CI_2(SO_3K)_2}$, is obtained by adding iodine (15 grams) in small quantities to a solution of the diazo-salt (20 grams in 120 grams of water), mixed with a solution of potassium hydrogen carbonate (22 grams in 88 grams of water); it crystallises from boiling water in lustrous, rectangular leaflets, and becomes yellow when exposed to light. Silver nitrate precipitates silver iodide from the boiling solution, but no change is produced in solutions of this or the foregoing salt by salts of other metals. Sodium amalgam converts both iodomethanedisulphonates into dipotassium methanedisulphonate.

*Basic potassium sulphohydrazimethylenedisulphonate*,



$$\mathrm{C(SO_3K)_2}{<}\begin{matrix}\mathrm{NK}\\ |\\ \mathrm{N{\cdot}SO_3K}\end{matrix}\mathrm{,H_2O,}$$

is obtained by gently heating the diazo-salt (30 parts) with a solution of potassium sulphite, prepared by neutralising with potassium carbonate (9—10 parts) a solution of hydrogen potassium sulphite (45 parts), formed by saturating a solution of caustic potash (1 : 5) with sulphurous anhydride. It is very soluble in water, forming an alkaline solution which yields a precipitate with barium chloride; this is dissolved by hydrochloric acid, and on heating the liquid, barium sulphate is thrown down, this being due to the quantitative elimination of the sulphonic group attached to nitrogen. When the salt is decomposed with sulphuric acid, hydrazine sulphate is formed, carbonic and sulphurous anhydrides being eliminated (compare Abstr., 1895, i, 647).



The *normal salt*, $C(SO_3K)_2{<}\begin{matrix}NH\\ |\\ N\cdot SO_3K\end{matrix},1\frac{1}{2}H_2O$, crystallises in small, lustrous prisms from a concentrated solution of the basic salt which has been saturated with glacial acetic acid. It is readily soluble in water, and the solution gives no precipitate with barium chloride.

*Hydroxymethanetrisulphonic acid*, $C(SO_3H)_3\cdot OH$, is obtained, in the form of its potassium salt, when the hydrazi-compound or the diazo-salt is treated with boiling water; the yield is more satisfactory when the latter is heated with a solution of hydrogen potassium sulphite. The potassium salt is identical with the compound described by Albrecht (*Annalen*, 1872, **161**, 139). The *barium* salt crystallises in lustrous leaflets, and contains $4H_2O$. M. O. F.

**Chloro-derivatives of αα-Dithienyl.** By OTTO EBERHARD (*Ber.*, 1895, **28**, 2385—2386).—Monochlorodithienyl, obtained by the action of concentrated sulphuric acid on monochlorothiophen (Abstr., 1894, i, 117) is converted by excess of sulphuryl chloride into *tetrachloro-αα-dithienyl*, $C_8H_2Cl_4S_2$; this crystallises in small, yellowish-brown needles, melting at 126·5—127° (corr.). When it is heated with two molecular proportions of sulphuryl chloride at 200°, it yields *perchlorodithienyl*, $C_8Cl_6S_2$, which forms long, reddish-yellow needles, melting at 211·5—212·5° (corr.). Tetrachlorodithienyl is converted by bromine into *tetrachlorodibromodithienyl*, $C_8Br_2\cdot Cl_4S_2$, which crystallises in hard yellowish needles, and melts at 189·5—190° (corr.). All these products can also be prepared from the synthetical αα-dithienyl, and this fact proves that the dithienyl derivatives previously described by the author belong to the same series. A. H.

**Synthesis of Aromatic Hydrocarbons.** By ALBERT TÖHL (*Ber.*, 1895, **28**, 2459—2463; compare Abstr., 1891, 1022; Töhl and Geyger, Abstr., 1892, 968; Töhl and Karchowski, Abstr., 1892, 990, and Jannasch and Wigner, Abstr., 1895, i, 655). In preparing parapropyltoluene by Fittig's method of synthesis, the author observed that propylic bromide gave a much better yield than the iodide. The author in conjunction with Tripke now shows that a fairly good yield of propylmesitylene may be obtained by the action of propylic bromide on mesitylic iodide, or still better on mesitylic bromide in the presence of sodium and ether. Ethylmesitylene has been obtained in a similar manner, but the yield is not so good as that obtained by Jannasch when working with a xylene solution. Cymene has also been synthesised in a similar manner by the action of sodium on isopropylic bromide and parabromotoluene.

*Propylmesitylene* boils at 220—221°, does not solidify at −20°, has a sp. gr. = 0·8773 at 20°, and when oxidised yields mesitylenecarboxylic acid (Jannasch and Weiler, Abstr., 1895, i, 283).

*Dibromopropylmesitylene* crystallises from alcohol in slender, long needles and melts at 56°.

*Barium propylmesitylenesulphonate*, $(C_{12}H_{17}SO_3)_2Ba + 2H_2O$, crystallises from water in small, glistening plates. The *sodium salt*, $C_{12}H_{17}\cdot SO_3Na + 2H_2O$, is readily soluble in water. The *calcium salt* crystallises with $1H_2O$, and the *magnesium salt* with $2H_2O$, but the *copper salt* is anhydrous. *Propylmesitylenesulphonamide* crystallises from concentrated solutions in small needles, which melt at 98—99°.

*Dinitropropylmesitylene*, obtained by dissolving the hydrocarbon in cold, fuming nitric acid, crystallises in small colourless needles, and melts at 93—94°. A substance, which melts at 135°, is also formed, but the constitution of this product has not yet been determined.

*Nitropropylmesitylene*, obtained by slowly dropping double the theoretical quantity of fuming nitric acid into the hydrocarbon, is an oily product, and on reduction yields *amidopropylmesitylene*, which is also an oil. The amido-compound yields a *sulphate*, which is readily soluble in water, crystallises in small needles and melts at 117°, and an *acetyl* derivative which melts at 161°.

Ethylmesitylene boils at 207—209° (uncorr.) whereas Jannasch gives 212—214° as the boiling point. *Dibromethylmesitylene*, $C_6Br_2Me_3Et$, melts at 219°, and the *dinitro-derivative*, $C_6Me_3Et(NO_2)_2$, at 123°. The *sulphonic acid* yields a *barium salt* which is very readily soluble in water, and also a *sodium salt*, $C_{11}H_{15}\cdot SO_3Na + H_2O$, which loses its water of crystallisation when kept over sulphuric acid.

J. J. S.

**Action of the Monobromo-derivatives of the Aromatic Hydrocarbons on the Lead Salts of the Thiophenols.** By Ed. Bourgeois (*Ber.*, 1895, **28**, 2312—2330).—When an aromatic monobromo-derivative is heated with the lead salt of an aromatic thiophenol, the latter dissolves at a temperature which is usually below 175°. When the solution is heated, action takes place in two stages; in the first between 180° and 190°, $2(RS)_2Pb + 4R'Br = (RS)_2Pb,PbBr_2 + RSR' + 2R'Br$, the double compound of the lead salt and lead bromide separate in the solid form, at a higher temperature, 225—230°, the reaction is completed in accordance with the equation $(RS)_2Pb,PbBr_2 + 2R'Br = RSR' + 2PbBr_2$. The author proposes to measure the velocity of the reaction during the first stage, which is undisturbed by secondary actions, and thus to obtain some idea as to the effect of the nature of the aromatic group on the power of the bromine atom to enter into reaction. The following new sulphides have been obtained by the above method in the course of the preliminary experiments.

All the sulphides when pure have a faint and not unpleasant odour, but acquire the usual smell of garlic when distilled. *Phenylic metatolylic sulphide* boils at 309·5°, and has the sp. gr. 1·1058 at 0°/4°. *Phenylic paratolylic sulphide* melts at 15·7°, boils at 311·5°, and has the sp. gr. 1·09 at its melting point. *as-Phenylic orthoxylylic sulphide*, ($Me_2 : S = 1 : 2 : 4$), boils at 181·5° (pressure = 11 mm.) and has the sp. gr. 1·0962 at 0°/4°. *as-Phenylic metaxylylic sulphide*, [$Me_2 : S = 1 : 3 : 4$], boils at 172·5° (pressure = 11 mm.) and has the sp. gr. 1·0935 at 0°/4°. *Phenylic paraxylylic sulphide* [$Me_2 : S = 1 : 4 : 2$] boils at 171° (pressure = 11 mm.) and has the sp. gr. 1·0913 at 0°/4°. *Phenylic mesitylic sulphide* boils at 180° (pressure = 11 mm.) and has the sp. gr. 1·0817 at 0°/4°. *Orthoparaditolylic sulphide* boils at 173° (pressure = 11 mm.) and has the sp. gr. 1·0889 at 0°/4°. *Metaparaditolylic sulphide* crystallises in lustrous needles, melts at 27·8°, and boils at 179° (pressure = 11 mm.). *Paratolylic orthoxylylic sulphide* [$Me_2 : S = 1 : 2 : 4$] forms crystalline granules melting at 28·6°. It boils at 193·7° (pressure = 11 mm.). *Paratolylic metaxylylic sulphide* [$Me_2 : S = 1 : 3 : 4$] boils at 188° (pressure = 11 mm.) and has the sp. gr. 1·0716 at 0°/4°. *Paratolylic paraxylylic sulphide*, [$Me_2 : S = 1 : 4 : 2$] melts at 6° and boils at 185° (pressure = 11 mm.). The liquid has the sp. gr. 1·072 at 0°/4°. *Paratolylic mesitylic sulphide* crystallises in small, lustrous needles, melts at 89·6°, and boils at 190° (pressure = 11 mm.). *Ortho-xylylic α-naphthylic sulphide* is a yellow liquid which boils at 246° (pressure = 11 mm.), and has the sp. gr. 1·1346 at 15°/4°. *Ortho-xylylic β-naphthylic sulphide* melts at 68° and boils at 251·5° (pressure = 11 mm.). *Metaxylylic α-naphthylic sulphide* is a yellowish liquid, which boils at 239·5° (pressure = 11 mm.) and has the sp. gr. 1·1355 at 15°/4°. *Metaxylylic β-naphthylic sulphide* crystallises in lustrous needles, melts at 39·6° and boils at 243·5° (pressure = 11 mm.). *Paraxylylic α-naphthylic sulphide* forms needles, melts at 36·2° and boils at 235° (pressure = 11 mm.). *Paraxylylic β-naphthylic sulphide* also forms needles, melts at 36·7° and boils at 240° (pressure = 11 mm.). *Mesitylic α-naphthylic sulphide* crystallises in large, lustrous tablets, melts at 120·6° and boils at 245° (pressure = 11 mm.). *Mesitylic β-naphthylic sulphide* crystallises in prisms melting at 87·5°, and boils at 245° (pressure = 11 mm.). The temperatures given are corrected. A. H.

**Potassium Derivatives of Quinone and Quinol.** By CHARLES ASTRE (*Compt. rend.*, 1895, **121**, 326—328).—When an ethereal solution of quinone is boiled with potassium, hydrogen is liberated, and the compound $C_6H_3KO(OH) + Et_2O$ is obtained as a deep green compound, which oxidises very rapidly when exposed to air, and becomes incandescent when heated at 100° or brought in contact with a mineral acid. In presence of benzene, the action of potassium on quinone yields quinhydrone and a brownish-green crystalline compound which oxidises with great rapidity, becomes incandescent in moist air, and takes fire if rubbed in presence of air. In contact with water, it is converted into a blue compound, which rapidly becomes brown; in contact with inorganic acids, it becomes incandescent. It seems to have the composition $C_{12}H_7O_4K_3$.

The action of potassium on quinol in presence of ether, yields a white, crystalline compound, $OH{\cdot}C_6H_4{\cdot}OK,C_6H_4(OH)_2$, which rapidly oxidises, and becomes first blue, then greyish-white, and finally very dark brown, in presence of moist air or oxygen.

The formation of these compounds supports the view that quinone is a diketone. C. H. B.

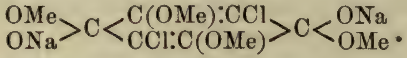
**Action of Sodium Alkyloxides on Chloranil. Acetals derived from Substituted Quinones.** By C. Loring Jackson and H. S. Grindley (*Amer. Chem. J.*, 1895, **17**, 579—607).—*Dichlorodiphenoxyquinone*, $C_6Cl_2O_2(OPh)_2$, is prepared by heating chloranil (25 grams) with an aqueous solution of phenol (25 grams) and potassium hydroxide (12 grams) on the water bath, and recrystallising the separated solid from benzene. It crystallises in aggregates of red needles, melts at 243°, and dissolves sparingly in alcohol, benzene, and chloroform, freely in hot glacial acetic acid, and not at all in water, ether, light petroleum, carbon bisulphide, or acetone. Caustic soda hydrolyses it, forming chloranilic acid. It is not reduced by sulphurous acid at 100°, but hydriodic acid converts it into *dichlorodiphenoxyquinol*. $C_6Cl_2(OH)_2(OPh)_2$, which crystallises in large colourless prisms and in arborescent needles, melts at 197—198°, and dissolves in most solvents except water, benzene, and light petroleum.

When warmed with aniline, dichlorodiphenoxyquinone yields dichlorodianilidoquinone.

*Tetrethylic dichloroquinonedimalonate*, $C_6Cl_2O_2[CH(COOEt)_2]_2$, is prepared by mixing dichlorodiphenoxyquinone with alcohol and ethylic sodiomalonate, when a dark blue precipitate separates; this is washed with alcohol, dissolved in water, and the solution treated with acid. The new compound crystallises in long, slender, stellate needles, melts at 132°, and dissolves in alcohol, but not in water. By reduction, it yields the corresponding quinol, already described by Stieglitz (Abstr., 1891, 455). As already indicated, the *sodio*-derivative $C_6Cl_2O_2[CNa(COOEt)_2]_2$, has a blue colour, and is soluble in water, but not in alcohol. When the quinone is boiled with sodium carbonate in absolute alcohol, *tetrethylic diethoxyquinonedimalonate*, $C_6O_2(OEt)_2[CH(COOEt)_2]_2$, is obtained; this forms nearly white crystals, melts at 115°, and dissolves in alcohol and ether, but not in water.

*Dichlorodimethoxyquinone dimethylhemiacetal*, $C_6Cl_2(OH)_2(OMe)_4$, is prepared by warming dichlorodiphenoxyquinone (10 grams) with a methylic alcohol solution of sodium (2·5 grams) methoxide; the white crystalline compound which separates, is dissolved in water and treated with dilute sulphuric acid, when the new compound is precipitated. The same compound is formed when chloranil is treated with a solution of sodium methoxide in methylic alcohol. It is a white, amorphous solid, insoluble in all common solvents, and is easily converted into dichlorodimethoxyquinone (methylic chloranilate, Abstr., 1890, 136) either by heat or by dilute acids; it is a feeble acid, forming a white crystalline compound with sodium methoxide. *Dichlorodiethoxyquinone diethylhemiacetal*, $C_6Cl_2(OH)_2(OEt)_4$, is similarly prepared, sodium ethoxide and ethylic alcohol being substituted for the methoxide and methylic alcohol respectively; it is a white, amorphous solid, which dissolves slightly in alcohol, but is partially decomposed thereby; it is insoluble in all other common solvents. At 140—143° it is converted into dichlorodiethoxyquinone (*loc. cit.*), and melts; dilute acids effect the same change. *Dichlorodimethoxyquinone diethylhemiacetal*, $C_6Cl_2(OMe)_2(OH)_2(OEt)_2$, was prepared from dichlorodimethoxyquinone and sodium ethoxide in alcoholic solution; it is similar in properties to the two preceding compounds.

The authors discuss the constitution of these hemiacetals in some detail. They find them to be incapable of reduction to quinols or of forming oximes with hydroxylamine hydrochloride, so that the ketonic character of the parent quinones has been lost; from this it is concluded that the sodium salt of dichlorodimethoxyquinone dimethylhemiacetal, for instance, has the constitution



$$\begin{matrix}\mathrm{OMe}\\ \mathrm{ONa}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{C(OMe){:}CCl}\\ \mathrm{CCl{:}C(OMe)}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{ONa}\\ \mathrm{OMe}\end{matrix}.$$

It is suggested that the constitution of phenoquinone and quinhydrone is similar to that of these hemiacetals. A. G. B.

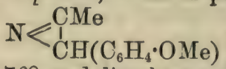
**Hydrolysis and Synthesis of Dihydroresorcinol.** By Daniel Vorländer (*Ber.*, 1895, **28**, 2348—2349; compare Abstr., 1894, i, 528).—It has been already shown (*loc. cit.*) that phenyldihydroresorcinol is converted into phenylacetylbutyric acid when treated with hydrolytic agents. The author finds that dihydroresorcinol behaves in the same way on subjection to similar treatment, yielding γ-acetylbutyric acid when heated with a concentrated solution of barium hydroxide during several hours at 150—160°; the *semicarbazone* dissolves with difficulty in water, and crystallises in lustrous leaflets melting at 164—166°.

The reaction by which dihydroresorcinol is converted into γ-acetylbutyric acid is reversible, dihydroresorcinol being produced when ethylic γ-acetylbutyrate is treated with sodium ethoxide; this is the simplest case of passing between the aromatic and aliphatic series.

Dihydroresorcinol is not formed by the action of ethylic sodacetoacetate on ethylic acrylate, the product being ethylic α-acetylglutarate. M. O. F.

**Action of Bromine on Anethoïl.** By Carl Hell and O. von Günthert (*J. pr. Chem.*, 1895, [2], **52**, 193—210; compare Abstr., 1895, i, 341).—In the preparation of bromanethoïl dibromide, the use of hot alcohol must be avoided, since, when hot, this solvent reacts with the dibromide, removing 1 mol. HBr, and forming a *compound* which crystallises in long prisms and melts at 62°. A study of the behaviour of the dibromide with hot water led to no definite conclusion.

When bromanethoïl dibromide is dissolved in aniline, aniline hydrobromide separates, and the filtrate from this yields a yellow powder, $C_{16}H_{16}OBrN$ (m. p. 75°), when decomposed by hydrochloric acid; this compound yields bromanisic acid when oxidised with potassium permanganate. The dibromo-ketone obtained by oxidising bromanethoïl dibromide (Abstr., 1895, i, 341) also yields an *aniline derivative*, $C_{16}H_{16}O_2BrN$, when heated with aniline; this crystallises in small aggregates of needles, melts at 119°, and dissolves easily in ether, alcohol, benzene, and chloroform, but only sparingly in light petroleum; it dissolves in strong sulphuric acid, and is precipitated unchanged therefrom by water; the compound appears to have been formed by the substitution of the aniline residue for the bromine atom of the side chain.

Anethoïl dibromide also yields a *ketone*, $C_{10}H_{11}BrO_2$, when oxidised with chromic acid in an acetic acid solution (compare *loc. cit.*); this forms large, strongly refractive crystals, melts at 65—67°, and dissolves in alcohol, ether, and light petroleum; the compound has a pungent odour, and burns the skin. When heated with alcoholic ammonia on the water bath, the ketone dissolves, and the solution leaves, when evaporated, a *compound*, which is probably an isoindole-like compound of the form  $N\left<\begin{matrix}CMe\\ | \\ CH(C_6H_4\cdot OMe)\end{matrix}\right.$; this is a yellow, crystalline powder, melts at 176°, and dissolves easily in ether, but only sparingly in alcohol, and not at all in light petroleum. Oxidation with potassium permanganate converts the ketone into anisic acid.

Two *dibromanethoïl dibromides*, $C_{10}H_{10}Br_4O$, were obtained by heating bromanethoïl dibromide with bromine (1 mol.) in a sealed tube; the one crystallises when the ethereal solution of the product of the action is evaporated, and forms slender needles which melt at 113—114°; the other remains as a syrup when the ether has been evaporated, and crystallises from this after a time; it melts at 89°, and is much more soluble in light petroleum than its isomeride. Reduction with zinc dust converts the dibromide into dibromanethoïl. The dibromide reacts with aniline to form the *compound* $C_{10}H_{15}OBr_2N$, which melts at 82°. Oxidation with chromic acid in acetic acid solution, converts the dibromide into a *ketone*, $C_{10}H_9Br_3O_2$, which contains two nucleal bromine atoms; it is a yellow powder, melts at 135°, and dissolves easily in ether, benzene, and chloroform. Two acids were extracted by sodium carbonate from the crude product of the oxidation of the dibromide; one of these melts at 85°, and is also formed when the ketone is oxidised by potassium permanganate; but neither has been identified. The *compound* $C_{10}H_9Br_2NO$, which is obtained by the action of alcoholic ammonia at 180° on the ketone, is insoluble in most organic solvents, and sublimes, without melting, at a high temperature. The behaviour of the ketone with aniline is also described.

A. G. B.

**The Cholesterols of Cryptogams.** By Ernest Gérard (*J. Pharm.*, 1895, [6], **1**, 601—608; compare Abstr., 1892, 1294).—The author has extracted cholesterol from ordinary brewer's yeast, from a common mould (*Mucor mucedo*), and from a lichen (*Lobaria pulmonacea*). The processes adopted in the three cases were similar.

Yeast (30 kilos.) containing 25—30 per cent. of solid matter is extracted with a large quantity of 96 per cent. alcohol. The residue, dried at 40—50°, and the aqueous solution left on distilling off the alcohol, are extracted with ether, and the combined ethereal extracts, which contain the cholesterol, together with the fatty matter and other substances, are evaporated to dryness; the cholesterol and fats are then extracted from this residue with light petroleum, and, after the removal of the solvent, are boiled with alcoholic potash to liberate the cholesterol. The alcohol having been removed, the cholesterol is extracted with ether from the aqueous alkaline soap solution, and the crystals thus obtained are washed with alcohol, and recrystallised from ether or benzene.

The cholesterol of yeast crystallises in rectangular plates or slender needles melting at 135—136°, and has a specific rotatory power, $[\alpha]_D = -105°$. No analysis is given. It is very sparingly soluble, even in boiling alcohol, but readily in the usual organic solvents. The benzoate could not be prepared in a pure state.

The mould was cultivated in a 6 per cent. solution of milk sugar containing the usual inorganic salts. Owing to the comparatively small amount of material available, the amount of cholesterol obtained was very minute, but it crystallised in plates, and appeared from its reactions to be identical with Tanret's ergosterine.

The product obtained from the lichen also crystallised in needles and plates, and exhibited similar reactions.

The cholesterol from cryptogams differs from animal cholesterol in its colour reactions with sulphuric acid. The latter gives a yellowish colour with the concentrated acid, which blackens on the addition of water, whilst under the same conditions the former gives a red colour, changing to blue. Similar colorations are yielded by carbon tetrachloride solutions of the cholesterol, with the exception that the yellow solution turns white instead of black; the chloroform solutions also exhibit analogous colour changes. JN. W.

**Electrolytic Reduction of Paranitro-compounds dissolved in Sulphuric acid.** By ARTHUR A. NOYES and JOHN J. DORRANCE (*Ber.*, 1895, **28**, 2349—2352; compare Abstr., 1893, i, 406; also 1894, i, 503).—A large platinum electrode is fitted closely to the side of a small beaker, in which is placed a porous cylinder containing a small platinum electrode; 20—30 grams of the nitro-compound is dissolved in two to three times its weight of concentrated sulphuric acid, and transferred to the beaker, whilst the porous cell, originally filled with concentrated sulphuric acid, is replenished from time to time with dilute acid. A current of 1 or 2 ampères is employed during 40—50 hours.

Paranitraniline yields paradiamidobenzene sulphate, paranitrophenol giving rise to paramidophenolsulphonic acid, which is also formed when parachloronitrobenzene is reduced.

The paper contains a short summary of the results hitherto obtained.

M. O. F.

**Action of Aniline on Mercurous Iodide.** By MAURICE FRANÇOIS (*Compt. rend.*, 1895, **121**, 253—256).—When mercurous iodide is mixed with excess of aniline in the cold, metallic mercury separates, and diphenyldimercurammonium iodide, $HgI_2,2NH_2Ph$, is formed and dissolves. At the boiling point of the aniline, the change takes place very rapidly. With aniline in smaller proportion, but still in excess, some of the mercurous iodide remains unchanged, and if mercuric iodide is dissolved in its own weight of warm aniline, and mercury is added, a small quantity of mercurous iodide forms on the surface of the metal. It follows that the action is, to a certain extent, reversible, and the author finds that when equilibrium is established at the boiling point of aniline, there are 26·35 parts of mercuric iodide in every 100 parts of the solution. The result is the same, whether the original substances are aniline and mercurous iodide, or aniline, mercuric iodide, and mercury. The quantity of mercuric iodide in solution when equilibrium is established varies with the temperature, but an exact determination was only made at the boiling point of the aniline.

A solution of mercuric iodide in aniline containing 26 parts of the salt in 100 parts of solution, does not decompose mercurous iodide at 182°, but dissolves it in considerable quantity, and the mercurous salt separates in crystals when the liquid is cooled, whilst the undissolved mercurous iodide, if the latter is in excess, is also found to have become crystalline. C. H. B.

**Halogen Additive Products of the Anilides.** By Henry L. Wheeler (*Amer. Chem. J.*, 1895, **17**, 612—619).—*Metanitracetanilide dibromide*, $C_8H_8N_2O_3Br_2$, is prepared by acting on metanitracetanilide in nitrobenzene with bromine, washing with light petroleum, and crystallising from chloroform. It forms stellate, yellow prisms, and melts and effervesces at 143°. Water removes hydrogen bromide from it, yielding *parabromometanitracetanilide*, which crystallises in yellow needles, and melts at 143°.

*Bromonitraniline*, $[NH_2 : NO_2 : Br = 1 : 3 : 4]$, is obtained when parabromometanitracetanilide is boiled with alcohol and strong hydrochloric acid. It crystallises in slender, yellow needles, and melts at 131°. Its *hydrochloride* and *sulphate* are described.

The author shows that in the above dibromide the bromine atoms are probably attached to the benzene nucleus, not to the nitrogen of the anilide group. A. G. B.

**Behaviour of Ethers of Azophenol on Reduction with Stannous Chloride and Hydrochloric acid.** By Paul Jacobson (*Annalen*, 1895, **287**, 97—147; compare Abstr., 1893, i, 327; and 1894, i, 26).—The paper forms an introduction to the matter brought forward in the following abstracts; it is divided into three portions, dealing respectively with the results of the investigation, their theoretical bearing, and the methods which have been adopted in the course of the work.

The changes involved when ethers of azophenol are reduced, follow three alternative courses, resulting in the formation of orthosemidine bases, parasemidine bases, and scission bases, the quantity in which bases of each class is produced being influenced by the nature of the azophenol derivative employed, and by the position in the molecule occupied by the substituent. The author has, therefore, collected in a table the quantitative results obtained on reducing various derivatives of benzeneazophenetoïl. M. O. F.

**Reduction of Benzeneazo-orthocresetoïl and Benzeneazometacresetoïl.** By Paul Jacobson, F. K. Fertsch, Fred. Marsden, and G. Schkolnik (*Annalen*, 1895, **287**, 147—160).—Benzeneazo-orthocresetoïl yields the orthosemidine base, 2 : 4 : 5-*amidoethoxy-*

*methyldiphenylamine*, $NH_2·C_6H_2Me(OEt)·NHPh$, which crystallises in lustrous leaflets, and melts at 94—95°; the *hydrochloride* is crystalline. The *azimide*, $C_{15}H_{15}N_3O$, is obtained by the action of nitrous acid on the base, and crystallises in colourless needles melting at 118°; the *methenyl* derivative, $C_{16}H_{16}N_2O$, formed on treating the base with boiling formic acid, crystallises from petroleum, and melts at 102°, whilst the *nitrate* and *hydrochloride* crystallise in needles. The *thiocarbenyl-compound*, $C_{16}H_{16}N_2OS$, is obtained by heating the base with carbon bisulphide and alcohol; it crystallises in small needles, softens at 225°, and melts at 238—240°. The *stilbazonium base*, $C_{29}H_{26}N_2O_2$, is obtained by condensation with benzile; it forms lustrous, lemon-yellow leaflets, and melts at 136°. *Monanilidotoluquinone* is obtained by oxidising the orthosemidine base with ferric chloride, and is also formed in preparing the azimide by treatment with nitrous acid; it crystallises from alcohol in lustrous, violet-red needles, and melts at 148°. *Dianilidotoluquinone* is produced when the foregoing substance is treated with aniline in alcoholic solution; it separates from glacial acetic acid in the form of a crystalline powder, and does not melt below 300°.

The orthosemidine base is not the sole product of reduction of benzeneazo-orthocresetoïl, a small quantity of a parasemidine base, 4-*amido*-4′ : 3′-*ethoxymethyldiphenylamine*, $NH_2·C_6H_4·NH·C_6H_3Me·OEt$, which crystallises from petroleum in lustrous, colourless needles, and melts at 110—111° being obtained; the *acetyl* derivative crystallises in rosettes of needles, and melts at 173°. From 10 grams of benzeneazo-orthocresetoïl, 4·95 grams of the orthosemidine base were obtained, the yield of the parasemidine base amounting to 2·1 grams, whilst 2 grams of scission bases were also formed.

*Benzeneazometacresetoïl*, $OEt·C_6H_3Me·N_2Ph$, crystallises in orange-red needles, and melts at 51·5°; the chief product of its reduction is the parasemidine base, 4-*amido*-4′ : 2′-*ethoxymethyldiphenylamine*, which crystallises from petroleum in pink prisms, and melts at 61°. The *monacetyl* derivative of this base melts at 97—98°; the *diacetyl* derivative at 153°. The *thiocarbamide* crystallises in nacreous leaflets, and melts at 181·5°. 4·7 grams of the parasemidine base were obtained from 10 grams of benzeneazometacresetoïl, 4·1 grams of mixed aniline and metacresetidine being formed at the same time.

M. O. F.

**Reduction of Ethers of Tolueneazophenols.** By PAUL JACOBSON, FR. DÜSTERBEHN, J. KLEIN, and G. SCHKOLNIK (*Annalen*, 1895, **287**, 161—183).—Reduction of orthotolueneazophenetoïl gives rise to the parasemidine base 4′ : 3 : 4′-*amidomethylethoxydiphenylamine* (D. R. P., 75,292), which crystallises from petroleum in colourless needles, and melts at 82°; the *hydrochloride* dissolves in cold water with extreme difficulty, and crystallises in leaflets. The *diazoiodide* is formed when a solution of the diazochloride is poured into aqueous potassium iodide, and crystallises in reddish-yellow needles. The *monacetyl* derivative melts at 156°, and the *diacetyl* derivative at 180—181°; the *benzylidene* derivative and *orthohydroxybenzylidene* derivative melt at 86—87° and 124—125° respectively. 4 : 4′ : 3-*Chlor-*

*ethoxymethyldiphenylamine* is obtained from the parasemidine base by Sandmeyer's reaction, and melts at 77—78°; the *nitrosamine* melts at 49—50°. From 10 grams of orthotolueneazophenetoïl, 5·1 grams of the parasemidine base were formed, 3·6 grams of a mixture of orthotoluidine and phenetidine being formed at the same time.

*Metatolueneazophenetoïl*, $C_6H_4Me{\cdot}N_2{\cdot}C_6H_4{\cdot}OEt$, crystallises from alcohol in orange-red prisms, and melts at 65°; on reduction, it yields approximately equal quantities (26—28 per cent.) of orthosemidine and parasemidine bases. The *hydrochloride* of the former, 2 : 5 : 3′-*amidoëthoxymethyldiphenylamine*, was isolated, but the base has not been obtained in the crystalline state; the *azimide* forms colourless needles, and melts at 110—111°, and the *stilbazonium base* crystallises in lustrous, yellow needles, and melts at 176°. The *methenyl* compound was obtained in the form of the *nitrate*, which crystallises in needles. The parasemidine base, 4 : 4′ : 2-*amidoethoxymethyldiphenylamine*, crystallises in long, colourless needles, which rapidly become blue when exposed to air, and melts at 92—93°; the *hydrochloride* crystallises from hot water in colourless leaflets, and the *monacetyl* derivative melts at 112—113°. An attempt has been made to obtain this base by synthetical means. 4′ : 2-*Ethoxymethyldiphenylamine* was prepared by the action of ethylic bromide and sodium ethoxide on hydroxymethyldiphenylamine; it separates from petroleum in pale yellow crystals, and melts at 81—82°, boiling under atmospheric pressure at 354° (uncorr.). The *nitrosamine* melts at 71—72°, but the transformation of this derivative into the parasemidine base has not been effected in a satisfactory manner.

Reduction of paratolueneazophenetoïl, which is first converted into paratoluenehydrazophenetoïl, gives rise to an orthosemidine base, which is either 2 : 5 : 4′-*amidoethoxymethyldiphenylamine*, or 2 : 4′ : 5-*amidoethoxymethyldiphenylamine*, in quantity amounting to 18 per cent., a mixture of paratoluidine and paraphenetidine being also produced to the extent of 69 per cent. Neither the hydrochloride nor the base has been analysed; the *azimide*, however, crystallises in colourless leaflets, and melts at 117—118°, and the *stilbazonium base* crystallises from alcohol in yellow needles, sinters at 141°, and melts at 144—146°.

When the isobutyl ether of paratolueneazophenol is reduced, 72 per cent. of the material employed, is obtained as a mixture of paratoluidine and the isobutyl ether of paramidophenol, the products of the semidine transformation not having been, in this case, examined. The benzyl ether of paratolueneazophenol yields paratoluidine and *paramidophenylic benzylic ether*, which crystallises in silky leaflets, and melts at 56° (Abstr., 1893, i, 330); the *acetyl* derivative melts at 139°. The mixture of these bases amounts to 78·5 per cent. of the material employed. M. O. F.

**Reduction of Tolueneazocresetoïls.** By Paul Jacobson, E. Heber, F. Henrich, and C. Schwarz (*Annalen*, 1895, **287**, 183—211).—Orthotolueneazo-orthocresetoïl crystallises in red, transparent aggregates, and melts at 35—37°; the difficulty with which it solidifies accounts for the observation of Noelting and Werner (Abstr., 1891, 214), who describe this substance as a red oil. On reduction, it yields the orthosemidine base, 2 : 5-*amidoethoxy*-2′ : 4-*dimethyldiphenylamine*, which crystallises in flat prisms, and melts at 78°; the *hydrochloride* is an oil which rapidly solidifies. The *thiocarbenyl-compound*, $C_{17}H_{18}N_2OS$, melts at 253°, and the *stilbazonium base* crystallises from alcohol in small, yellow needles, and melts at 153°. Oxidation with ferric chloride converts the orthosemidine base into *orthotoluidotoluqinone*, which crystallises in dark, lustrous leaflets, and melts at 145—146°. The parasemidine base, 4 : 4′ : 3 : 3′-*amidoethoxydimethyldiphenylamine*, is also formed on the reduction of orthotolueneorthocresetoïl; it crystallises in colourless leaflets, becomes red when exposed to air, and melts at 86°. The *monacetyl* derivative melts at 143°, the *thiocarbamide* at 179—180°, and the *diformyl* derivative at 146—147°. The ortho- and para-semidine bases are obtained in quantities amounting to 29 and 36 per cent. respectively, the remainder of the product consisting of scission bases.

*Metatolueneazo-orthocresol*, $C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot OH$ [N : Me : OH = 1 : 3 : 4], is obtained by bringing together diazotoluene chloride and orthocresol in molecular proportion; it crystallises from benzene in lustrous, golden yellow needles, and melts at 115°. *Metatolueneazo-orthocresetoïl* crystallises in reddish-yellow plates, and melts at 46—47°. When this ether is reduced, the orthosemidine base, 2 : 5-*amidoethoxy*-3′ : 4-*dimethyldiphenylamine*, is produced in quantity amounting to 43 per cent. of the material employed; it crystallises from petroleum in aggregates of colourless needles, and melts at 91—91·5°. The *azimide* crystallises from petroleum in leaflets, and melts at 83—84°; the *stilbazonium base* melts 137·5—140°, and the solution in alcohol exhibits greenish-yellow fluorescence. Oxidation with ferric chloride converts the orthosemidine base into *metatoluidotoluquinone*, which forms purple-red needles, and melts at 142°. The parasemidine base, 4 : 4′ : 2 : 3′-*amidoethoxydimethyldiphenylamine*, is also formed when metatolueneazo-orthocresetoïl is reduced, the yield amounting to rather more than 5 per cent. It crystallises from petroleum in long needles, and melts at 99—100°.

Reduction of paratolueneazo-orthocresetoïl gives rise to the orthosemidine base, 2 : 5 : 4 : 4′-*amidoethoxydimethyldiphenylamine*, which crystallises from dilute alcohol in small, white needles, which become violet when exposed to light or air, and melt at 76°. The *azimide* crystallises in colourless leaflets, and melts at 131°, the *thiocarbenyl-compound* at 205—206°, and the *stilbazonium base* at 146—149°. The yield of the orthosemidine base amounts to 50 per cent., 21 per cent. of mixed bases being also obtained.

*Orthotolueneazometacresol* crystallises in orange-red plates, and melts at 112°; the *sodium* derivative crystallises in lustrous, yellow leaflets. *Metacresolbisazo-orthotoluene*, $(C_6H_4Me\cdot N_2)_2C_6H_2Me\cdot OH$, is formed during the preparation of the phenol, and melts at 188°. *Orthotolueneazometacresetoïl* crystallises from alcohol in deep red, lustrous needles, and melts at 64°; when this substance is reduced 43 per cent. of the parasemidine base, 4 : 4′ : 3 : 2′-*amidoethoxydimethyldiphenylamine*, is formed, 53 per cent. of other bases being produced at the same time. The base crystallises in white leaflets, and melts at 86°; the *sulphate* crystallises from alcohol in long, colourless needles, and the *monacetyl* derivative and *diacetyl* derivative melt at 144° and 115° respectively.

*Metatolueneazometacresol* crystallises in orange-yellow, rhombic plates, and melts at 106—107°; during its preparation *metacresolbisazometatoluene* is formed, crystallising in long, reddish-brown needles, and melting at 102—103°. *Metatolueneazometacresetoïl* crystallises from alcohol in red prisms, and melts at 73°; on reduction, it yields 44 per cent. of the parasemidine base, 4 : 4′ : 2 : 2′-*amidoethoxydimethyldiphenylamine*, which crystallises in colourless prisms from benzene to which petroleum has been added; it melts at 95—96°, the *monacetyl* derivative at 116°, and the *thiocarbamide* at 70—72°.

*Paratolueneazometacresol* crystallises from benzene in orange-red prisms, and melts at 135°; *metacresolbisazoparatoluene* is formed at the same time, and melts at 107°. *Paratolueneazometacresetoïl* crystallises from alcohol in orange-red, four-sided plates, and melts at 64°; on reduction, it yields 24 per cent. of an orthosemidine *base*. The *stilbazonium base* crystallises in long, canary-yellow needles, and melts 178—179°. M. O. F.

**Reduction of Metaxyleneazophenetoïl.** By PAUL JACOBSON and G. SCHKOLNIK (*Annalen*, 1895, **287**, 211—212).—*Metaxyleneazophenol* crystallises from benzene in brown prisms, and melts at 134°. *Metaxyleneazophenetoïl* crystallises in red needles, and melts at 97°. On reducing this substance, 74 per cent. of mixed bases is obtained, consisting of xylidine and phenetidine. M. O. F.

**Reduction of Azophenetoïls.** By PAUL JACOBSON and FRIEDRICH MEYER (*Annalen*, 1895, **287**, 212—220).—*Orthophenetoïlazoparaphenol*, $OEt{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$, is obtained by adding a solution of diazotised phenetidine to a well-cooled solution of sodium phenoxide containing 1 gram of phenol to 25 grams of water; it crystallises from benzene in lustrous, reddish-brown leaflets, and melts at 131°. *Orthophenetoïlazoparaphenetoïl* crystallises from alcohol in brown leaflets with a golden lustre, and melts at 77—78°. When this substance is reduced, the parasemidine base, 4 : 3 : 4′-*amidodiethoxydiphenylamine*, is obtained; this crystallises from petroleum in lustrous, feathery leaflets, and melts at 84·5°; the *hydrochloride* forms aggregates of colourless needles, which rapidly become blue. The *thiocarbamide* melts at 154·5—155°. The parasemidine base is obtained in quantity amounting to 51 per cent. of the material employed.

*Metaphenetoïlazoparaphenol* melts at 105—106°, *metaphenetoïlparaphenetoïl* at 70—71°; on reduction, the latter yields 69 per cent. of a mixture consisting of ortho- and para-semidine bases.

*Paraphenetoïlazoparaphenol* melts at 125—126°, and not at 104·5° as already stated (D. R. P., 48,543). On reducing the ethyl ether, 95 per cent. of paraphenetidine was obtained. M. O. F.

**Constitution of the Hydroxyazo-compounds.** By WILLIAM McPHERSON (*Ber.*, 1895, **28**, 2414—2418).—Two views have been held with regard to the constitution of the hydroxyazo-compounds;

one that their constitution is that denoted by the name, the other that they are in reality quinone-derivatives. Benzoquinone reacts with phenylhydrazine and its alkyl derivatives to form quinol, free nitrogen, and other products. With $\beta$-benzoylphenylhydrazine, however, it reacts like a ketone, *quinonemonophenylbenzoylhydrazone*,

$$C_6H_4O{:}N{\cdot}NPhBz,$$

being formed. This substance crystallises in yellowish needles, or in groups of flat prisms, which melt at 171°. It is quantitatively converted by zinc dust and acetic acid into benzanilide and paramidophenol; this reaction is exactly similar to that shown by many of the acetic and benzoic derivatives of the orthohydroxyazo-compounds.

Quinonebenzoylhydrazone explodes when it is brought in contact with phenylhydrazine, and even in alcoholic solution a vigorous action, accompanied by evolution of nitrogen, takes place. Quinonebenzoylhydrazone, which from its properties and the method by which it is obtained, must have the formula given above, is entirely different in its properties from the benzoate of parahydroxyazobenzene (*Ber.*, **6**, 561), which is hydrolysed by concentrated sulphuric acid or alcoholic potash into benzoic acid and parahydroxyazobenzene, and therefore appears to have the formula $OBz{\cdot}C_6H_4{\cdot}N{:}NPh$. This true hydroxyazo-compound is converted by zinc dust and acetic acid into a dihydrogen derivative, which is probably the corresponding hydrazo-compound.

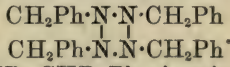
Quinonebenzoylhydrazone, like the benzoate of parahydroxyazobenzene, is converted by sulphuric acid or alcoholic potash into benzoic acid and parahydroxyazobenzene, so that the two isomeric benzoic derivatives yield, on hydrolysis, only one compound (compare Nef, *Annalen*, **287**, 354).

These results seem to show that parahydroxyazobenzene really has the constitution indicated by its name, and is a true hydroxy-derivative and not a quinone derivative. The research is being extended to the naphthalene derivatives. A. H.

**Rules controlling the Formation of Azo-colouring Matters.** By WILHELM VAUBEL (*J. pr. Chem.*, 1895, [2], **52**, 284—288).—The author points out that the formation of azo-colouring matters may be well compared with the bromination of aromatic hydroxy- and amido-compounds. Such differences as are noticeable may be traced to the closer relationship of the amido-group to the azo-group than to the hydroxyl-group, and to the smaller acidifying power of the azo-group as compared with that of the bromine atom, as well as in the spacial relationship of the azo-group towards the bromine atom. It must further be noted that bromination takes place in acid solution, whilst the formation of azo-dyes is generally effected in alkaline or neutral solutions, seldom in the presence of acids. A. G. B.

**Symmetrical Dibenzylhydrazine (Hydraziphenylmethane).** By THEODOR CURTIUS and E. QUEDENFELDT (*Ber.*, 1895, **28**, 2345—2347; compare Abstr., 1889, 393).—*Symmetrical dibenzylhydrazine*, $CH_2Ph{\cdot}NH{\cdot}NH{\cdot}CH_2Ph$, is obtained by reducing benzylideneazine in alcoholic solution with sodium amalgam; it crystallises in large, lustrous plates, and melts at 65°. On remaining exposed to the atmosphere, it becomes converted into a colourless oil. The base is indifferent towards alcohol, water, acids, and alkalis, and does not reduce Fehling's solution; it reduces a cold, ammoniacal silver solution however. The *monohydrochloride* is not decomposed on exposure to air; it crystallises in colourless prisms, and melts at 153°. The *picrate* is insoluble in water, but crystallises from alcohol in long, golden-yellow prisms, and melts at 130°. The *acetyl* derivative crystallises in colourless needles, and melts at 78°; the *benzoyl* derivative melts at 87°, and the *nitroso*-derivative, which crystallises from alcohol in large, yellow prisms, at 89°. When the nitroso-derivative is treated with reducing agents, ammonia is formed, together with dibenzylhydrazine or benzylamine, according as reduction is mild or energetic.

Oxidation of dibenzylhydrazine in alcoholic solution with mercuric oxide, leads to the formation of a *compound* which crystallises from alcohol in colourless prisms, and melts at 152°; although having the empirical formula of azobenzyl, its molecular weight is found to be twice as great, and it probably has the constitution



$$\begin{array}{c}CH_2Ph\cdot N\cdot N\cdot CH_2Ph\\ \;\;|\;\;\;| \\ CH_2Ph\cdot N.N\cdot CH_2Ph\end{array}.$$

*Benzylideneazine tetrabromide*, CHBrPh·NBr·NBr·CHBrPh, is obtained by adding bromine to a chloroform solution of benzylideneazine; it forms orange-red crystals, and melts at 134°. On dissolving it in acetone, a colourless liquid is obtained, bromacetone and the *dihydrobromide* of benzylideneazine being formed. Liberation of nitrogen takes place when benzylideneazine tetrabromide is dissolved in alcohol; the reaction proceeds quantitatively, mineral acids and boiling water producing the same effect. M. O. F.

**Tautomerism.** By WILLY MARCKWALD (*Annalen*, 1895, **286**, 343—368; compare Abstr., 1895, i, 347).—The author is of opinion that the amidines are tautomeric compounds, and that the hypothesis of pseudomerism cannot be applied to them. Derivatives of this class would be expected to behave consistently with having both the structures NHR′·CR:NR″ and NR′:CR·NHR″; this is actually the case, and where contradictions have occurred in the apparent existence of two isomerides, repetition of the experiments in question has established their inaccuracy. The author criticises von Pechmann's views regarding the constitution of formazyl-compounds (Abstr., 1894, i, 456), and discusses the subject of tautomerism at some length.

In the formulæ given below it is to be understood that the tautomeric formula is also implied in each case.

*Orthoparaditolylacetamidine*, $C_6H_4Me\cdot N:CMe\cdot NH\cdot C_6H_4Me$, is obtained from ethylisothioacetorthotoluidide and paratoluidine, or from ethylisothioacetoparatoluidide and orthotoluidine (Wallach and Wüsten, *Ber.*, 1883, **16**, 148). It crystallises from alcohol in needles, and melts at 144—145°; the same product is obtained from both sources, and the previous investigators were mistaken in recognising two modifications.

Phenylparatolylbenzamidine (von Pechmann, Abstr., 1895, i, 347) is obtained from benzanilide imidochloride and paratoluidine, or from benzoparatoluidide imidochloride and aniline; the two forms originally described by von Pechmann are identical, as he, himself, has since shown (*loc. cit.*), and both preparations, when recrystallised, melt at 131—132° to a turbid liquid, which becomes clear at 133°. The *nitrate* forms small, white crystals, and melts and decomposes at 144°; the *hydrochloride* melts at 237°, and the picrate at 195°.

Diphenylparatolylguanidine, $C_6H_4Me\cdot N:C(NHPh)_2$, is formed from aniline and phenyltolylcyanamide; aniline, phenyltolylthiocarbamide, and lead oxide; paratoluidine, diphenylthiocarbamide, and lead oxide, or from paratoluidine and diphenylcyanamide; Huhn, by means of the first two methods, obtained products which he believed to be different from one another (Abstr., 1886, 1036). The base separates from alcohol in white crystals, and melts at 128—129°; the *hydrochloride* melts at 221—222°, and the *platinochloride* becomes brown at 230°, but does not melt at this temperature.

*Tetraphenglparatolyldiguanide*,

$$NHPh\cdot C(NPh)\cdot N(C_6H_4Me)\cdot C(NPh)\cdot NHPh,$$

is obtained as a bye-product in preparing the foregoing compound from diphenylcyanamide and paratoluidine; it crystallises from absolute alcohol, and melts at 150°. It is prepared by allowing the latter substance to remain in alcoholic solution with the former (2 mols.) for one day. The *hydrochloride* melts and decomposes at 156°, and the *platinochloride* melts at 136°.

*Pentaphenyldiguanide*, $NHPh\cdot C(NPh)\cdot NPh\cdot C(NPh)\cdot NHPh$, is a bye-product in the preparation of triphenylguanidine; it is also prepared by allowing an alcoholic solution of aniline and diphenylcyanamide to remain for one day at the ordinary temperature. It melts at 160°, and when heated with aniline yields triphenylguanidine. The *hydrochloride* melts at 213°, and the *platinochloride* is amorphous.

Phenyldiorthotolylguanidine, $NPh:C(NH\cdot C_6H_4Me)_2$, was described by Huhn, who obtained a product melting at 102° from diorthotolylcyanamide and aniline, and from diorthotolylthiocarbamide, aniline, and lead oxide, whilst a preparation from phenylorthotolylcyanamide and orthotoluidine, or from phenylorthotolylthiocarbamide and orthotoluidine by the action of lead oxide, melted at 112°. Making use of these four methods, the author has been able to isolate one form only of phenyldiorthotolylguanidine; this separates from alcohol in well-formed, colourless crystals, and melts at 97—98°; the *hydrochloride* melts at 197°, and the *nitrate* melts and decomposes at 183°; the *platinochloride* forms minute orange-yellow crystals, and melts at 213—214°. When the base is prepared by either of the methods indicated, tritolylguanidine (m. p. 130—131°) is formed at the same time; its *hydrochloride* melts above 250°, and the *nitrate* decomposes and melts at 204°. The action of carbon bisulphide on phenyldiorthotolylguanidine affords evidence of the tautomeric nature of this substance; if its structure is to be represented by the tautomeric formulæ $NPh:C(NH\cdot C_6H_4Me)\cdot NH\cdot C_6H_4Me$ and

$$NHPh\cdot C(NH\cdot C_6H_4Me):N\cdot C_6H_4Me,$$

a mixture of diorthotolylthiocarbamide and phenylthiocarbimide with phenylorthotolylthiocarbamide and orthotolylthiocarbimide should be formed under the influence of carbon bisulphide, whilst a substance having a rigid structure would yield only one thiocarbamide and one thiocarbimide. Experiment shows that the former alternative takes place, irrespective of the source from which the base is derived.

*Diphenylorthotolylguanidine*, $C_6H_4Me\cdot N{:}C(NHPh)_2$, is the sole product of the action of orthotoluidine on diphenylcyanamide; it separates from alcohol in white crystals, and melts at 112°. The *nitrate* melts at 172°, and the *platinochloride* at 210°.

*Tetraorthotolylphenyldiguanide*,

$$C_6H_4Me\cdot NH\cdot C(N\cdot C_6H_4Me)\cdot NPh\cdot C(N\cdot C_6H_4Me)\cdot NH\cdot C_6H_4Me,$$

is obtained by the union of aniline with diorthotolylcyanamide (2 mols.); it crystallises from alcohol in white needles, and melts at 111°. The *hydrochloride* and the *platinochloride* are sparingly soluble in water. M. O. F.

**Mixed Amidines and Tautomerism.** By HANS VON PECHMANN (*Ber.*, 1895, **28**, 2362—2374; compare Abstr., 1895, i, 347).—Former experiments have dealt with the tautomerism of the types $NX{:}R\cdot NHY$ and $NHX\cdot R{:}NY$, in which X and Y represent chemically similar radicles; in the present series, the radicles are dissimilar, and it is found in consequence that tautomerism does not occur.

*Methylbenzamide imidochloride*, $CPhCl{:}NMe$, is obtained by the action of phosphorus pentachloride on methylbenzamide; it is a colourless, mobile liquid which has an irritating odour, and boils at 124° under a pressure of 60 mm., undergoing slight decomposition.

*β-Naphthylamidobenzenylmethylimidine*, $NMe{:}CPh\cdot NH\cdot C_{10}H_7$, is obtained by allowing β-naphthylamine to act on the foregoing substance dissolved in ether, or from β-benzonaphthalide imidochloride and methylamine. It separates from much boiling alcohol in lustrous crystals, and melts at 204°. The crystalline form is monosymmetric, $a:b:c = 1{\cdot}8456:1:0{\cdot}70848$; $\beta = 81{\cdot}39°$. The *picrate* crystallises in sulphur-yellow prisms, and melts at 166·5°.

*β-Naphthylmethylamidobenzenylmethylimidine*,

$$NMe{:}CPh\cdot NMe\cdot C_{10}H_7,$$

is obtained by methylating the foregoing substance, and is identical with the amidine obtained from methylbenzamide imidochloride and β-methylnaphthylamine; it is an oil which readily forms the *picrate*, crystallising in orange-yellow plates, melting at 155·5°.

*Dimethylamidobenzenyl-β-naphthylimidine*. $Me_2N\cdot CPh{:}NC_{10}H_7$, is formed when dimethylamine remains in contact with benzonaphthalide imidochloride; the *hydriodide* crystallises from ether in colourless prisms, and melts at 215°, whilst the *picrate* forms bright yellow prisms, and melts at 150°.

*Phenylamidobenzenylmethylimidine*, $MeN{:}CPh\cdot NHPh$, is obtained by the action of aniline on methylbenzamide imidochloride, and of methylamine on benzanilide imidochloride; it crystallises from alcohol in colourless needles, and melts at 134°. The *picrate* melts at 169°, and the *hydriodide* at 190°.

*Methylphenylamidobenzenylmethylimidine*, $MeN{:}CPh{\cdot}NMePh$, is produced on methylating the foregoing substance; it crystallises from petroleum, and melts at 56°. The *hydriodide* is colourless, and melts at 190°; the *picrate* melts at 174°.

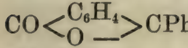
*Dimethylamidobenzenylphenylimidine*, $Me_2N{\cdot}CPh{:}NPh$, is obtained from benzanilide imidochloride and dimethylamine; it melts at 73—74°. The *hydriodide* forms lustrous prisms, and melts at 196°; the *picrate* melts at 126°.

*Phenylamidobenzenylanilimidine*, $NHPh{\cdot}CPh{:}N{\cdot}NHPh$, is obtained by heating a mixture of benzanilide imidochloride and phenylhydrazine on the water bath; it crystallises in yellow prisms, and melts at 119°. Ferric chloride develops a red coloration in the alcoholic solution; in concentrated sulphuric acid, the same coloration is developed by potassium dichromate, whilst ferric chloride produces no change. Fehling's solution is slowly reduced on boiling. The *hydrochloride* is sparingly soluble, and crystallises in needles, and the *picrate* melts and decomposes at 202°.

*Anilamidobenzenylphenylimidine*, $PhN{:}CPh{\cdot}NH{\cdot}NHPh$, is produced by heating a solution of benzophenylhydrazide imidochloride in benzene with aniline, and also in the preparation of the foregoing base; it crystallises in lustrous needles, and melts at 174—175°. Ferric chloride develops a brown coloration in the alcoholic solution, and a violet coloration in concentrated sulphuric acid solution; Fehling's solution is reduced on boiling. The *hydrochloride* is readily soluble, and crystallises in needles; the *picrate* melts and decomposes at 175°. M. O. F.

**Action of Phenylic Isocyanate on some Acids and Ethereal Salts.** By ALBIN HALLER (*Compt. rend.*, 1895, **121**, 189—193).—Phenylic isocyanate and cyanacetic acid, in molecular proportion, react at the ordinary temperature, and yield *cyanacetanilide*, $CN{\cdot}CH_2{\cdot}CO{\cdot}NHPh$, which crystallises from alcohol in nacreous white plates melting at 199°. Methylsalicylic acid and phenylic isocyanate at 120° yield *methylsalicylanilide*, which melts at 62°, and is not affected by water or by boiling aqueous potash. Anisic acid, on the other hand, at 120°, yields anisic anhydride, identical with that obtained by the action of phosphorus oxychloride on sodium anisate; at 180—190°, however, it yields anisanilide. Anisic acid, therefore, behaves in the same manner as benzoic, toluic, phthalic, camphoric, and other acids (Abstr., 1895, i, 679). Phenylglycollic acid yields only phenylglycollamide, $OH{\cdot}CHPh{\cdot}CO{\cdot}NHPh$, melting at 145—146°.

Benzoylbenzoic acid and phenylic isocyanate, in presence of ether or light petroleum, yield unstable crystals, which readily split up into their proximate constituents when dissolved in any hot neutral solvent. If, however, the two compounds are heated at 100° in the absence of any solvent, symmetrical diphenylcarbamide and benzoylbenzoic acid are formed; the latter crystallises from alcohol in transparent, lozenge-shaped crystals melting at 140—141°, and is identical with the anhydride obtained by von Pechmann by heating acetylbenzoylbenzoic anhydride at 200°, this product melting at 140—141°, and not at 120°, as stated by Pechmann.

At 140—150°, benzoylbenzoic acid and phenylic isocyanate seem to yield benzoylbenzanilide, but the latter could not be isolated. It follows that benzoylbenzoic acid behaves both as a lactone-alcohol,  $CO<\substack{C_6H_4\\O\text{———}}>CPh\cdot OH$, and as an acid ketone, $COOH\cdot C_6H_4\cdot COPh$.

Ethylic tartrate and phenylic isocyanate, in presence of dry benzene, at 130° yield the compound

$$COOEt\cdot C(OH)(CO\cdot NHPh)\cdot C(OH)(CONHPh)\cdot COOEt,$$

which crystallises from benzene in white needles melting at 164°, and, when dissolved in chloroform, has a molecular rotatory power $[\alpha]_D = -61\cdot 56°$. C. H. B.

**Action of Benzoic Chloride on Urethane.** By HANS VON PECHMANN and LUDWIG VANINO (*Ber.*, 1895, **28**, 2383—2384).—Benzoylurethane is obtained by heating a mixture of urethane, benzoic chloride, and pyridine, in molecular proportion, for 10—12 hours in boiling water; the mass is agitated with caustic soda and ether, and the alkaline liquid acidified. A solution of the product in alcohol deposits *ethylic benzoylallophanate*, $COPh\cdot NH\cdot CO\cdot NH\cdot COOEt$, which crystallises in silky needles, and melts at 179° (compare Kretschmar, *Ber.*, 1875, **8**, 104), whilst benzoylurethane (m. p. 110°) crystallises from the mother liquor. When ethylic benzoylallophanate is heated above its melting point, it solidifies at 200—205°, phenylic cyanide distilling over; the residue crystallises from alcohol in lustrous leaflets, and melts at 223°. M. O. F.

**Syntheses with Sodamide Derivatives.** By CARL BLACHER (*Ber.*, 1895, **28**, 2352—2360; compare Abstr., 1895, i, 289).—The author has continued his study of sodamide derivatives, and included sodium succinimide and sodium phthalimide in the investigation.

Sodium succinimide yields benzylsuccinimide when heated with excess of benzylic chloride for four hours in a reflux apparatus; sodium acetanilide gives rise to acetobenzylanilide. Benzoic anhydride and acetic anhydride yield with sodium benzamide, dibenzamide and acetylbenzamide respectively; diacetanilide is formed when acetic anhydride acts on sodium acetanilide.

The action of sodium or potassium ethylic sulphate on sodium benzamide and sodium phthalimide leads to the formation of ethylbenzamide and ethylphthalimide respectively. M. O. F.

**Ethereal Imidocarbonates and the so-called Normal Ethereal Cyanates.** By ARTHUR R. HANTZSCH and LUDWIG MAI (*Ber.*, 1895, **28**, 2466—2472).—The authors agree with Nef (*Annalen*, **287**, 310) in stating that the ethereal salts of cyanic acid described by Cloez (*Annalen*, **102**, 355) have no existence. The products of the reaction between cyanogen chloride and sodium alkyloxides consist mainly of the ethereal salts of imido-carbonic acid (as much as

92 per cent.), together with small quantities of etheral salts of cyanuric acid.

*Phenylic imidocarbonate*, $NH{:}C(OPh)_2$, is most readily obtained by the action of cyanogen bromide (1 mol.) on a mixture of sodium phenoxide (1 mol.) and phenol (1 mol.), dissolved in ether. It forms a hard, white mass, melts at 54°, and readily undergoes decomposition even at the ordinary temperature, yielding phenylic cyanurate and phenol. The decomposition takes place much more rapidly when the solution of the phenylic imidocarbonate in light petroleum is heated for several hours.

By no alterations in the methods of procedure, were the authors enabled to obtain normal phenylic cyanate.

*Parabromophenylic imidocarbonate*, $NH{:}C(O{\cdot}C_6H_4Br)_2$, is readily obtained by the action of parabromophenol (2 mols.) on cyanogen bromide (1 mol.); it melts at 129°, is sparingly soluble in ether and cold alcohol, and is also more stable than the corresponding phenylic salt.

*Ethylic imidocarbonate* is very stable, and is only decomposed into alcohol and ethylic cyanurate when heated in sealed tubes at 200° for several hours. Aqueous solutions of the imido-ether, when treated with an alkaline solution of bromine, give a precipitate of *ethylic bromimidocarbonate*, $NBr{:}C(OEt)_2$; this is readily soluble in ether, and crystallises in needles, which melt at 43°.

No trace of ethylic cyanate could be obtained by the action of cyanogen bromide on sodium ethoxide, nor yet of methylic cyanate from sodium methoxide. The chief product was always the imido-ether, together with small quantities of the cyanurate.

Sodium phenoxide and also sodium parabromophenoxide cause the condensation of phenylic isocyanate into phenylic isocyanurate. The polymeride of phenylic isocyanate obtained by Hofmann (*Annalen*, **1**, 57) differs from this cyanurate, and is shown to be a dimolecular isocyanate, whereas the isocyanurate is a tri-molecular compound.

J. J. S.

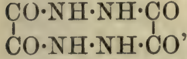
**Benzazide (Benzoylazoimide). Acid Azides of the Fatty Series.** By Theodor Curtius (*J. pr. Chem.*, 1895, [2], **52**, 210—226; compare Abstr., 1895, i, 32).—Benzoylazoimide (benzazide) (Abstr., 1891, 56) is best purified by dissolving it in acetone, from which it crystallises in large, colourless tables melting at 32°. Its behaviour with water, with alcohol, with bromine, and with aniline has been described (Abstr., 1894, i, 331; 1895, i, 32). Dimetanitrodiphenylcarbamide melts at 247—250°, not at 233° as heretofore stated.

When reduced by means of sodium amalgam in alcohol, benzoylazoimide is converted into ethylic benzoate and sodium azoimide; when alcoholic ammonium sulphide is the reducing agent, benzamide and ammonium azoimide are the products, hydrogen sulphide being liberated. When zinc dust and glacial acetic acid are used, benzamide can alone be isolated; but when caustic soda is substituted for acetic acid, sodium benzoate and sodium azoimide are formed, unless the solution is very dilute, when nitrogen is evolved and dibenzoylhydrazine (m. p. 233°), $NHBz{\cdot}NHBz$, produced (compare *loc. cit.*).

Phenylazoimide, $PhN_3$, can be similarly reduced to hydrazobenzene, $NHPh{\cdot}NHPh$, by sodium amalgam in alcohol.

*Succinylazoimide*, $C_2H_4(CO{\cdot}N_3)_2$, is prepared by gradually adding sodium nitrite (2 mols.) to a well cooled, concentrated aqueous solution of succinylhydrazine hydrochloride (Abstr., 1895, i, 264), and shaking with ether. It crystallises in long prisms, and explodes when heated. It is easily soluble in alcohol, sparingly so in ether, and insoluble in water. Under water, it melts at 30°. Boiling water decomposes it with evolution of carbonic anhydride and nitrogen, and formation of ethylenecarbamide. Boiling alcohol decomposes it, with formation of ethylenediurethane (m. p. 110°).

Attempts to prepare oxalylazoimide, $N_3{\cdot}CO{\cdot}CO{\cdot}N_3$, have not been successful; treatment of oxalylhydrazide (*loc. cit.*) in the manner described in the preceding paragraph, yielded *hydrazioxalyl*,



$\begin{array}{l} CO{\cdot}NH{\cdot}NH{\cdot}CO \\ | \qquad\qquad\quad\; | \\ CO{\cdot}NH{\cdot}NH{\cdot}CO \end{array}$, which is a white solid, insoluble in all solvents.

*Malonylazoimide*, $CH_2(CO{\cdot}N_3)_2$, prepared by diazotising malonylhydrazine (*loc. cit.*) in the manner described for succinylhydrazide, is an explosive oil which is converted into a yellow oil when heated with alcohol; the reactions of the yellow oil prove it to be methylenediurethane.

*Glycolylazoimide*, $OH{\cdot}CH_2{\cdot}CO{\cdot}N_3$, is easily obtained by diazotising glycolylhydrazine (Abstr., 1895, i, 331) hydrochloride; it crystallises in double pyramids, and explodes feebly. Boiling alcohol converts it into the *urethane*, $OH{\cdot}CH_2{\cdot}NH{\cdot}COOEt$, which melts at 189°.

A. G. B.

**Azides (Azoimides) of Substituted Benzoic acids.** By A. Struve and Rudolf Radenhausen (*J. pr. Chem.*, 1895, [2], **52**, 227—242).—*Metanitrobenzoylazoimide*, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}N_3$, is prepared by dissolving metanitrobenzoylhydrazine in dilute nitric acid, and adding the calculated quantity of sodium nitrite. It crystallises in white laminæ, melts at 68°, and dissolves easily in ether, benzene, alcohol, and glacial acetic acid, but not in water. It is also the main product of the action between diazobenzene sulphate and metanitrobenzoylhydrazine. When heated with much water, it is converted into dimetanitrodiphenylcarbamide melting at 234° (compare preceding abstract). *Tetranitrodiphenylcarbamide* crystallises in yellow needles. When metanitrobenzoylazoimide is boiled with alcohol, it yields *metanitrophenylurethane*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}COOEt$, which crystallises in yellow needles, melts at 56°, and dissolves easily in alcohol and ether; strong hydrochloric acid at 120° decomposes it into carbonic anhydride, alcohol, and metanitraniline.

*Orthonitrobenzoylazoimide* is similarly prepared; it crystallises in yellow prisms, melts at 36°, and dissolves freely in ether, chloroform, and benzene, but only sparingly in light petroleum.

*Paranitrobenzoylazoimide* crystallises in colourless laminæ, melts at 69°, and resembles the meta-derivative in solubility. Hot water converts it into *diparanitrodiphenylcarbamide*, $CO(NH{\cdot}C_6H_4{\cdot}NO_2)_2$, which crystallises in lemon-yellow needles, melts above 260°, and is insoluble in water; hydrochloric acid at 130° decomposes it with formation of paranitraniline, but the change is more difficult to accomplish than in the case of the meta-derivative. Hot alcohol converts paranitrobenzoylazoimide into paranitrophenylurethane (Abstr., 1885, 149).

*Orthobromobenzoylhydrazine*, $C_6H_4Br{\cdot}CO{\cdot}NH{\cdot}NH_2$, from ethylic orthobromobenzoate and hydrazine hydrate, crystallises in colourless needles, melts at 153°, and is only sparingly soluble in water, but freely so in alcohol and hot benzene.

*Metahydroxybenzoylhydrazine*, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}NH_2$, from ethylic metahydroxybenzoate and hydrazine hydrate, forms white crystals, melts at 150°, and dissolves in water and alcohol, but not in ether, chloroform, or benzene. When its aqueous solution is shaken with benzaldehyde, *benzylidenemetahydroxybenzoylhydrazine*,

$$OH{\cdot}C_6H_4CO{\cdot}NH{\cdot}N{:}CHPh,$$

separates; it melts at 205°.

*Metahydroxybenzoylazoimide*, $OH{\cdot}O_6H_4{\cdot}CO{\cdot}N_3$, prepared by diazotising the hydrazine, forms small, nearly colourless crystals, melts at 95°, and dissolves easily in alcohol, ether, and chloroform, but only sparingly in light petroleum; when heated with water, it yields *dimetahydroxydiphenylcarbamide*, $CO(NH{\cdot}C_6H_4{\cdot}OH)_2$, which forms colourless crystals, and melts at 220°.

*Parahydroxybenzoylhydrazine*, prepared like the meta-derivative, crystallises in white laminæ, melts at 260°, and dissolves in hot water and alcohol. The corresponding *benzylidene* derivative forms white crystals, and melts at 218°. *Parahydroxybenzoylazoimide* crystallises in white needles, melts at 132°, and dissolves in ether, alcohol, benzene, and chloroform, but not in water. When it is heated with alcohol, it yields a crystalline compound which melts at 105—110°, and is converted by hot water into *diparahydroxydiphenylcarbamide;* this crystallises in colourless needles, and decomposes, without melting, at 230°.

*Orthohydroxybenzoylhydrazine*, prepared from methylic salicylate and hydrazine hydrate, crystallises in colourless laminæ, and melts at 145°. The corresponding *benzylidene* derivative forms small, colourless crystals, and melts at 230°. *Orthohydroxybenzoylazoimide* crystallises in large, colourless, rhombic plates, melts at 27°, and has a powerful, tear-exciting odour. *Diorthohydroxydiphenylcarbamide* crystallises in white needles, and melts at 125°.

*Metamidobenzoylhydrazine*, $NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}NH_2$, is prepared from ethylic metamidobenzoate and hydrazine hydrate. It forms colourless crystals, melts at 77°, and is very soluble in cold water and in alcohol; the *hydrochloride*, $NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}N_2H_3,2HCl$, melts at 265°. The *benzylidene* derivative, $NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh$, melts at 180°. *Metamidobenzoylazoimide*, $NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}N_3$, is precipitated by adding sodium acetate to a mixture of metamidobenzoylhydrazine and diazobenzene sulphate in aqueous solution; it crystallises in yellow needles, melts at 85°, and dissolves in ether, benzene, and light petroleum.

A. G. B.

**Hydrazide and Azoimide of Hippuric Acid.** By Theodor Curtius (*J. pr. Chem.*, 1895, [2], **52**, 243—271).—The author describes in detail the preparation of hippurylhydrazine (Abstr., 1891, 56; 1892, 112; 1895, 32) by the action of hydrazine hydrate on (1) ethylic hippurate, (2) hippuramide, (3) hippurylazoimide, (4) ethylic hippurylglycolate.

*Hippurylhydrazine hydrochloride*, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot NH_2,HCl$, forms colourless crystals. The *platinosochloride*,

$$(NHBz\cdot CH_2\cdot CO\cdot NH\cdot NH_2)_2PtCl_2,$$

crystallises in slender needles. Hippurylbenzylidenehydrazone has previously been described (Abstr., 1891, 56). *Hippurylcinnamylidenehydrazine*, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot N{:}CH\cdot CH{:}CHPh$, crystallises in yellowish prisms, and melts at 201·5°. *Symmetrical acetylhippurylhydrazine*, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot NHAc$, is formed by the interaction of acetylhydrazine (Abstr., 1895, 263) with hippurylazoimide in ethereal solution; it crystallises in colourless needles, melts at 186°, and dissolves easily in alcohol. *Symmetrical hippurylphenylhydrazine*, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot NHPh$, from phenylhydrazine and hippurylazoimide, crystallises in silvery laminæ or needles, melts at 182·5°, and can be distilled nearly undecomposed when quickly heated; it dissolves in hot alcohol, but not in water or in ether; it does not reduce hot Fehling's solution. *Nitrosohippurylphenylhydrazine*, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot NPh\cdot NO$, prepared by treating the last-named compound in glacial acetic acid solution with sodium nitrite, forms a yellow, crystalline powder, melts at 128—129°, and dissolves in alcohol, but not in water; hot water decomposes it into phenylazoimide and hippuric acid. *Acetylhippurylphenylhydrazine*,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot NPhAc,$$

prepared by digesting hippurylphenylhydrazine with acetic anhydride, forms a white, crystalline powder, melts at 155°, and dissolves in water and alcohol, but not in ether. *Dihippurylhydrazine*, $(NHBz\cdot CH_2\cdot CO)_2N_2H_2$, can be prepared by heating a mixture of hippurylhydrazine and ethylic hippurate in molecular proportion; it forms small, silvery crystals, melts at 268—269°, and is insoluble in boiling alcohol, boiling water, and ether; it is a feeble acid.

*Hippurylazoimide*, $NHBz\cdot CH_2\cdot CO\cdot N_3$, the product of the action of sodium nitrite and acetic acid on an aqueous solution of hippurylhydrazine, has been previously described as a nitrosohippurylhydrazine (Abstr., 1891, 57), and as diazohippuramide (Abstr., 1892, 113); new analyses have now established its identity. It does not give Liebermann's reaction, as previously stated, neither does it give a precipitate with silver nitrate in alcoholic solution until some time has elapsed, when silver azoimide separates. With alkalis, hippurylazoimide yields the alkali azoimide and the alkali hippurate, but as an intermediate product a salt is obtained which has a blue fluorescence (compare *loc. cit.*). With acids, hippurylazoimide is hydrolysed into hippuric acid and azoimide, whilst with ammonia it yields ammonium azoimide and hippuramide. This reaction with ammonia is typical of the behaviour of hippurylazoimide with aniline, paratoluidine, and metatoluylenediamine; the following new compounds have been prepared by such reactions.

*Hippuranilide* crystallises in long, lustrous prisms, melts at 208·5°, and dissolves easily in hot glacial acetic acid and hot alcohol, but only sparingly in cold alcohol or ether, and not at all in cold water. *Nitrosohippuranilide*, $NHBz{\cdot}CH_2{\cdot}CO{\cdot}NPh{\cdot}NO$, obtained by the action of nitrous acid on the anilide, is a yellowish, crystalline powder, which darkens below 100°, and melts between 195° and 197°.

*Hippuroparatoluidide*, $NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$, crystallises in colourless needles, and dissolves freely in hot alcohol and hot glacial acetic acid, but only sparingly in water, cold alcohol, or ether.

*Hippuroparatoluylenediamide*, $NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH_2$, crystallises in pale yellow, lustrous laminæ, melts at 205°, and shows a similar solubility to that of hippuroparatoluidide.

The behaviour of hippurylazoimide with hydrazine and acid hydrazides has already been indicated (Abstr., 1895, 34), and the products of these reactions will be described in a future communication.

In discussing the behaviour of hippurazide with water, alcohol, and halogens (compare Abstr., 1894, i, 331; 1895, 32; this vol., i, 34), the author adopts the name *hippenyl* for the radicle $NHBz{\cdot}CH_2$—.

*Dihippenylcarbamide*, $(NHBz{\cdot}CH_2{\cdot}NH)_2CO$, is obtained when hippurylazoimide is boiled with water, carbonic anhydride and nitrogen being eliminated. It forms microscopic, colourless crystals, melts at 246°, and is nearly insoluble in water, but dissolves to some extent in hot alcohol and glacial acetic acid. Hydrochloric acid, at 120°, converts it into benzoic acid, ammonium chloride, carbonic anhydride, and formaldehyde. When the hot filtrate from the dihippenylcarbamide is cooled, a compound, probably *hippenylcarbanil*,

$$NHBz{\cdot}CH_2{\cdot}N{:}CO,$$

or a polymeride thereof, separates in the form of colourless crystals, which melt at 233°; dilute acids readily decompose it into benzoic acid, ammonia, formaldehyde, and carbonic anhydride. A third *compound*, $C_9H_6N_2O$, is left as an oil when the mother liquor from the carbanil is evaporated; it is soluble in alcohol and in glacial acetic acid, from which it is precipitated in the form of crystals; it melts at 98°. The same substance is produced when hippurylazoimide is heated either by itself or in an indifferent medium.

Hippurylazoimide reacts with alcohols at their boiling points to form the corresponding hippenylurethanes; these are hydrolysed by hydrochloric acid, at 100°, into benzoic acid, ammonia, formaldehyde, carbonic anhydride, and the parent alcohol. *Hippenylethylurethane*, $NHBz{\cdot}CH_2{\cdot}NH{\cdot}COOEt$, crystallises in aggregates of colourless needles, melts at 162°, and dissolves easily in hot alcohol, benzene, and glacial acetic acid, but only sparingly in hot water. It behaves as a base, and can be distilled almost unchanged. *Hippenylmethylurethane*, $NHBz{\cdot}CH_2{\cdot}NH{\cdot}COOMe$, crystallises like the ethyl compound, and melts at the same temperature (162°). *Hippenylbenzylurethane*, $NHBz{\cdot}CH_2{\cdot}NH{\cdot}COO{\cdot}CH_2Ph$, crystallises in felted needles, which become highly electrified by friction; it also melts at 162°. Both the last-named compounds resemble the ethyl compound in properties.

Alkylic haloïd salts react with moist hippurylazoimide, when warmed therewith, to form the corresponding hippenylurethane, with liberation of hydrogen haloïd. In this reaction, the author sees evidence that moist hippurylazoimide has the constitution

$$NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N_2{\cdot}OH.$$

By treating hippurylazoimide with a halogen in ethereal solution, nitrogen is eliminated, and a dihaloïdhippenylcarbanil is formed. In this way, compounds which are assumed to be *dibromohippenylcarbanil*, $NHBz{\cdot}CH_2{\cdot}NBr_2{:}CO$, and *diiodohippenylcarbanil* have been crystallised.

Reactions of hippurylazoimide with hydrogen chloride, aldehyde, and acid amides, are briefly mentioned, but their elucidation will receive further attention. A. G. B.

**Appendix to recent Publications (Benzoylhydrazines).** By Theodor Curtius (*J. pr. Chem.*, 1895, [2], **52**, 272—276).—In describing carbohydrazimine, Curtius and Dedichen (Abstr., 1895, i, 29) have overlooked the fact that Angeli (Abstr., 1894, i, 149) had previously prepared the same compound. The compounds described as hydrazimines in the same paper are wrongly named; they contain two fewer hydrogen atoms, and are identical with Pinner's isodihydrotetrazines (*Ber.*, 1889, **22**, 3274). The author thinks Purgotti's claim for priority (Abstr., 1895, i, 27) cannot be allowed.

*Ethylic benzoylhydrazoneacetoacetate*, $COPh{\cdot}NH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}COOEt$ (compare Struve, Abstr., 1895, i, 34), has been prepared by heating benzoylhydrazine with ethylic acetoacetate; the crude material melts at about 60°, but when its solution in alcohol is diluted, it separates as an oil, which is still liquid at −15°.

The preparation of ethylic metanitrobenzoylhydrazoneacetoacetate (Abstr., 1895, i, 276) is detailed. A. G. B.

**Metallic Bisulphite Compounds of Aldehydes.** By A. Fagard (*J. Pharm.*, 1895, **6**, [2], 145—148).—*Benzaldehyde lithium hydrogen sulphite*, $C_7H_6O,LiHSO_3 + \frac{1}{2}H_2O$, is prepared by passing sulphurous anhydride into an aqueous suspension of lithium carbonate, into which benzaldehyde is slowly dropped. The product is evaporated to crystallisation, preferably under low pressure. The sulphate crystallises in small, colourless prisms, and appears to resemble the analogous sodium compound.

*Acetone barium hydrogen sulphite*, $2C_3H_6O,Ba(SO_3H)_2,H_2O$, is made by passing sulphurous anhydride into a mixture of barium hydroxide, water, and acetone. The baryta gradually dissolves, with evolution of heat, and the additive compound separates on cooling. It crystallises in small, brilliant plates, resembling those of boric acid.

The corresponding *strontium* compound is anhydrous, and forms small needles, or twinned prisms. Jn. W.

**Resolution of Benzaldehydecyanhydrin by means of Alkalis.** By Carl Glücksmann (*Chem. Centr.*, 1895, i, 273—274, from *Pharm. Post.*, **27**, 573—574 and 585—588; compare E. Utescher, Abstr., 1895, i, 419).—The fact that benzaldehyde combines with hydrocyanic acid in dilute solution has no bearing on the question of the hydrolysis of benzaldehydecyanhydrin, since this is treated successively with alkali, acid, and silver nitrate. The action of magnesium hydroxide is, like that of potash, direct; it is not dependent on the formation of silver oxide, and the hydrolysis is completed more rapidly. J. B. T.

**Parahydroxybenzaldehyde.** By Carl Paal (*Ber.*, 1895, **28**, 2407—2414).—The monobromo- and moniodo-derivatives of parahydroxybenzaldehyde described by Herzfeld (*Ber.*, **10**, 2196) are in reality disubstitution products. Bromine converts parahydroxybenzaldehyde, when dissolved in dilute alcohol, directly into the dibromo-derivative, whilst, if chloroform be used as the solvent, *metabromoparahydroxybenzaldehyde* [CHO : Br : OH = 1 : 3 : 4] can readily be obtained. It crystallises from hot water in white plates, melts at 124°, and decomposes when distilled. The *sodium* and *silver* derivatives crystallise in needles. *Metabromoparahydroxybenzaldoxime* crystallises in druses of white needles, melting at 135°. *Metabromoparahydroxybenzylideneaniline* forms flat needles, melting at 135°. *Metabromoparahydroxybenzoic acid* is formed by the oxidation of the aldehyde with alkaline permanganate; it crystallises in concentric groups of white, flat needles, melting at 148°, and is soluble in hot water. *Metiodoparahydroxybenzaldehyde* is found in the mother liquors obtained in the preparation of the di-iodo-derivative. It crystallises in white plates, but has not yet been obtained quite pure.

Metanitroparahydroxybenzaldehyde can be readily prepared by dissolving the hydroxybenzaldehyde in acetic acid and adding nitric acid. A. H.

**Ketones.** By Heinrich Limpricht (*Annalen*, 1895, **286**, 306—342).—The ketones described in the following abstracts were prepared by mixing the chloride employed with a slight excess of the hydrocarbon, adding several volumes of carbon bisulphide, and heating the liquid with aluminium chloride in a reflux apparatus for 8—12 hours. The ketone is obtained as a resinous cake, and, after being washed with water, is crystallised from alcohol.

The carbonyl group in these ketones occupies the para-position with respect to the methyl of the tolyl residue. M. O. F.

**Metanitrophenyl Paratolyl Ketone.** By Heinrich Limpricht and M. Lenz (*Annalen*, 1895, **286**, 307—321).—*Metanitrophenyl paratolyl ketone* crystallises in white leaflets, and melts at 111°; in small quantities, it may be distilled without undergoing decomposition. The ketone is readily soluble in organic solvents and hot alcohol, but is sparingly soluble in cold alcohol and 50 per cent. acetic acid. The *dichloride* is obtained as a brown oil by heating it with phosphorus pentachloride; the ketone is regenerated on treating this substance with alcoholic ammonia or aniline. The *monochloro*-derivative is formed when chlorine gas is led into the ketone at 150°; it crystallises from alcohol in long, brittle needles, and melts at 96°. The *monobromo*-derivative crystallises from alcohol in long, white needles, and melts at 116°. *Metanitrophenyl-paratolyl-ketonesulphonic acid* is obtained by dissolving the ketone in several volumes of fuming sulphuric acid; it crystallises from water in large, rhombic plates containing $3H_2O$. The substance effloresces in the atmosphere, and melts at 140° with effervescence, but if heated for eight hours in the vapour of boiling toluene it becomes anhydrous, and then melts at 215°; the *barium* salt crystallises from water in colourless prisms, and contains $3H_2O$. *Dinitrophenyl paratolyl ketone* forms white scales, and melts at 125°; the *trinitro*-derivative crystallises in minute, six-sided prisms, and melts at 165°. *Azoxyphenyl paratolyl ketone* is prepared by dissolving the nitroketone in alcoholic potash; it separates from alcohol in yellow crystals, and melts at 145°. The *ketoxime*, obtained by heating the alcoholic solution of the ketone with hydroxylamine hydrochloride and sodium carbonate, crystallises from alcohol in white, lustrous needles, melting at 111°; if caustic soda is employed, the *ketoxime* of the azoxy-derivative is formed, occurring in two modifications which melt at 235° and 245° respectively.

*Metamidophenyl paratolyl ketone* is obtained by reducing the nitroketone in alcoholic solution with stannous chloride; it crystallises from alcohol in amber-coloured prisms, melts at 111°, and may be distilled in small quantities without undergoing decomposition. The *hydrochloride* crystallises in needles, and melts at 198°; the *sulphate* separates from water in aggregates of needles, and melts at 142°. The *sulphonic acid* of the amido-ketone forms small crystals which decrepitate when heated; it melts at 300°, and effervesces and blackens. The *acetyl*-derivative crystallises in small, white prisms, and melts at 139°. On adding sodium nitrite to an aqueous solution of the amidoketone sulphate, the *diazo*-compound is formed: gas is evolved when the diluted liquid is boiled, and the slender, white needles which the cold solution deposits melt at 120°, and consist probably of hydroxyphenyl paratolyl ketone. Phenyl paratolyl ketone is obtained from the amido-ketone by adding a concentrated aqueous solution of sodium nitrite to a solution of the hydrochloride in absolute alcohol, and treating the liquid with finely divided copper. The *ketoxime* of amidophenyl paratoyl ketone crystallises in minute, white prisms, and melts at 146°; the amido-ketone is regenerated on heating it with concentrated hydrochloric acid for four hours.

*Metanitroparabenzoylbenzoic acid*, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, is obtained by oxidising the nitro-ketone, in glacial acetic acid solution, with chromic anhydride; it crystallises in rhombic tables, melts at 242°, and sublimes at higher temperatures, forming white crystals. The *potassium* salt crystallises in white needles, and the barium salt, containing $1H_2O$, forms leaflets; the *chloride* melts at 94°, and the *amide* at 204°. *Metamidoparabenzoylbenzoic acid* is obtained by reducing the foregoing nitro-compound with stannous chloride; it crystallises from alcohol, and contains $1H_2O$, which is lost at 145°, when the substance melts; the *barium* salt is anhydrous, the *hydrochloride* crystallises in long, slender needles, melting above 250°, and the *sulphate* contains $2H_2O$. When the chloride of nitrobenzoylbenzoic acid is heated with toluene and aluminium chloride, *metanitrophenyl paratolylphenylene diketone*, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4Me$, is formed; it crystallises in colourless leaflets, and melts at 210°. When oxidised with chromic anhydride in glacial acetic acid solution, it yields *metanitroparabenzoylparabenzoylbenzoic acid*,

$$NO_2\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot COOH,$$

which melts at 276°; the *sodium* salt crystallises in nacreous scales.

M. O. F.

**Paranitrophenyl Paratolyl Ketone.** By HEINRICH LIMPRICHT and E. SAMIETZ (*Annalen*, 1895, **286**, 321—332).—*Paranitrophenyl paratolyl ketone* crystallises in white needles, and melts at 122—124°. In small quantities, it may be sublimed without undergoing decomposition; the ketone is soluble in organic solvents and in concentrated sulphuric acid. *Dinitrophenyl paratolyl ketone* melts at 127°, and *trinitrophenyl paratolyl ketone* at 159°; both these compounds have been obtained by Milne (*Ber.*, 1874, **7**, 983), and they appear to be identical with the dinitro- and trinitro-ketones described in the foregoing abstract.

*Paramidophenyl paratolyl ketone* is obtained by reducing an alcoholic solution of the nitro-compound with stannous chloride; it separates from benzene in well-formed crystals, and melts at 179°. The *sulphate* forms nacreous leaflets, and melts and decomposes at 210—216°; the *acetyl* derivative melts at 155°. On adding sulphuric acid and sodium nitrite to an alcoholic solution, the amido-ketone becomes diazotised; copper powder is then added, and on filtering the liquid into water, separation of phenyl paratolyl ketone (m. p. 52°) takes place. *Diamidophenyl paratolyl ketone* is obtained by reducing the dinitro-compound, and melts at 178°; the *sulphate* becomes dark, and decomposes above 240°. *Triamidophenyl paratolyl ketone* crystallises from water in white needles, which become brown on exposure to air; it melts at 199°.

*Parahydroxyphenyl paratolyl ketone* is obtained by boiling an aqueous solution of the diazotised amido-ketone; it crystallises in long, white needles, and melts at 160°. *Bromophenyl paratolyl ketone* is prepared by treating the diazo-compound with hydrogen bromide and copper powder; it crystallises in small, white needles, and melts at 139°. The *ketoxime* of paranitrophenyl paratolyl ketone crystallises in aggregates of needles, and melts at 145°; the *phenylhydrazone* crystallises in lustrous, scarlet needles, and melts at 154°. The *phenylhydrazone* of the amido-ketone forms lustrous, brownish-red, rhombic crystals, and melts at 163°.

*Paranitroparabenzoylbenzoic acid* is obtained by oxidising paranitrophenyl paratolyl ketone with chromic anhydride in glacial acetic acid solution; it melts at 255°. The *sodium* salt crystallises in small, anhydrous leaflets; the *chloride* melts at 124°. *Paramidoparabenzoylbenzoic acid* crystallises in bright yellow needles, and melts at 211°; the *sulphate* is colourless and anhydrous.

*Paranitrophenyl paratolylphenylene diketone*,

$$NO_2\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO\cdot C_6H_4Me.$$

is obtained from toluene and the chloride of paranitroparabenzoylbenzoic acid by treatment with aluminium chloride; it melts at 236°. *Paranitroparabenzoylparabenzoylbenzoic acid* crystallises in lustrous leaflets, and melts at 306—308°; the *sodium* salt dissolves sparingly in water.

M. O. F.

**Metanitrophenylxylyl Ketones.** By HEINRICH LIMPRICHT and H. FALKENBERG (*Annalen*, 1895, **286**, 333—342).—*Metanitrophenyl metaxylyl ketone* crystallises in lustrous yellow leaflets and melts at 64°. The *trinitro*-derivative crystallises from alcohol in yellow needles and melts at 138—139°.

*Metamidophenyl metaxylyl ketone* is obtained by reducing the nitro-compound with stannous chloride; it forms brownish crystals and melts at 118°. The *hydrochloride* crystallises in needles and the *sulphate* in lustrous nodules. The *sulphonic acid* of metanitrophenyl metaxlyl ketone crystallises from water in long, white, lustrous needles; the *barium* salt contains $2H_2O$, which is lost at 130°. *Azoxyphenyl metaxylyl ketone* is prepared by treating the nitro-ketone with boiling alcoholic potash; it separates from petroleum in small, red needles and melts at 124°. The *ketoxime* of metanitrophenyl metaxylyl ketone forms small, white crystals, and melts between 131° and 149°.

Two *metanitrobenzoylmetatoluic acids*, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_3Me{\cdot}COOH$, are obtained by oxidising the nitro-ketone with chromic anhydride in glacial acetic acid solution, melting at 173° and 152—153° respectively. The *barium* salt of the former is anhydrous, and crystallises in yellow needles and the *silver* salt forms minute white prisms, becoming violet when exposed in the moist state to light; the *chloride* is an oil, and the amide forms yellowish-brown crystals and melts at 226°.

*Metanitrophenyl orthoxylyl ketone* crystallises in yellow plates belonging to the rhombic system, and melts at 100°. *Metamidophenyl orthoxylyl ketone* is very soluble in alcohol and ether; the *sulphate* crystallises in pale-red nodules, and the *hydrochloride* forms white needles.

*Metanitrobenzoylorthotoluic acid* forms small, yellowish crystals and melts at 191°; the *barium* salt crystallises in yellow needles, and the *silver* salt is also crystalline, becoming violet when exposed to light in the moist condition.

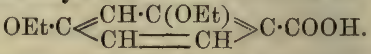
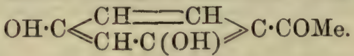
*Metanitrophenyl paraxylyl ketone* forms white, silky crystals, and melts at 97—98°. *Metamidophenyl paraxlyl ketone* was not obtained in the crystalline state; the *sulphate* forms reddish crystals, and the *hydrochloride* crystallises in yellowish needles.

*Metanitrophenylparatoluic acid* crystallises from glacial acetic acid in lustrous, brownish needles, and melts at 189°; the *barium* salt forms small, yellow crystals, and the moist *silver* salt is decomposed by light.

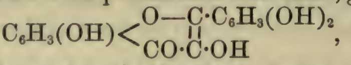
M. O. F.

**Resacetophenone.** By GEORG GREGOR (*Monatsh.*, 1895, **16**, 619—629; compare Nencki and Sieber, Abstr., 1881, 591; Wechsler, Abstr., 1894, i, 521, and Glücksmann, Abstr., 1892, 38).—When diethylresacetophenone (1 mol.) is suspended in water and oxidised by the gradual addition of a solution containing potassium permanganate (1 mol. $K_2Mn_2O_8$) and potassium hydroxide (2 mols.), 2 : 3-*diethoxybenzoylformic acid*, $C_6H_3(OEt)_2{\cdot}CO{\cdot}COOH$, is formed. It is insoluble in cold water but dissolves in hot water, and more readily in alcohol and ether; from the solution in benzene, it separates in small crystals which melt at 127°. It forms an *oxime*, $C_{12}H_{14}O_4{:}NOH$, which crystallises from benzene and melts and decomposes at 130°, a *silver* salt, $C_{12}H_{13}AgO_5$, which is amorphous, a *sodium* salt, $C_{12}H_{13}NaO_5 + 6H_2O$, which crystallises in scales, and a crystalline *barium* salt,

$$(C_{12}H_{13}O_5)_2Ba + 8H_2O.$$

On reduction with sodium amalgam, the alcoholic acid, $C_{12}H_{16}O_5$, is formed. This crystallises from benzene, melts at 115°, forms the *silver salt*, $C_{12}H_{15}AgO_5$, and is oxidised by permanganate in dilute acid solution to an acid identical with the product of oxidation of Tiemann and Lewy's diethylresorcylaldehyde, which is therefore unsymmetrical diethoxybenzoic acid,  $\mathrm{OEt{\cdot}C}\lessdot{\mathrm{CH{\cdot}C(OEt)} \atop \mathrm{CH{=\!=}CH}}\gtrdot\mathrm{C{\cdot}COOH}$. The author therefore concludes that resacetophenone has the constitution  $\mathrm{OH{\cdot}C}\lessdot{\mathrm{CH{=\!=}CH} \atop \mathrm{CH{\cdot}C(OH)}}\gtrdot\mathrm{C{\cdot}COMe}$.

G. T. M.

**Constitution of Fisetin.** By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1895, **28**, 2302—2309; compare Abstr., 1894, i, 93).—Two constitutional formulæ are possible for fisetin, which is converted by fusion with potash into resorcinol, glycollic acid and protocatechuic acid,  $C_6H_3(OH)<{\mathrm{O{-}C{\cdot}}C_6H_3(OH)_2 \atop \mathrm{CO{\cdot}C{\cdot}OH}}$, [OH : O : CO = 1 : 5 : 6 or 1 : 3 : 4]. When tetraethylfisetin is boiled with alcoholic potash, it yields diethylprotocatechuic acid and diethyl fisetol ether, which, if fisetin have the second of the above formulæ, must have the formula, $OEt{\cdot}C_6H_3(OH){\cdot}CO{\cdot}CH_2{\cdot}OEt$ [= 1 : 3 : 4], according to which it is an ethoxy-derivative of monethyl resacetophenone ether. On oxidation, diethyl fisetol ether is converted into ethyl-β-resorcylic acid (Herzig, Abstr., 1891, 1386). The authors have now shown that ethyl resacetophenone ether yields exactly the same product and have thus confirmed the accuracy of the view that the second of the above formulæ represents the constitution of fisetin. When resacetophenone is treated with alcoholic potash and ethylic iodide, it yields a mixture of the two ethers. *Diethyl resacetophenone ether* crystallises in quadratic prisms melting at 74—75°. *Ethyl resacetophenone ether*, $OEt{\cdot}C_6H_3(OH)CO{\cdot}CH_2{\cdot}OEt$, separates from dilute alcohol in white plates melting at 49°. On oxidation, the latter of these compounds is converted into ethyl-β-resorcylic acid, identical with that obtained by Herzig from diethyl fisetol ether, and with that prepared by the authors from β-resorcylic acid.

Benzoylresorcinol differs from resacetophenone in its behaviour towards alcoholic potash and methylic iodide, *benzoylmethylresorcinol*, $C_6H_2MeBz(OH)_2$, being formed. This substance crystallises in faintly yellow lustrous plates, melting at 176°; it does not contain a methoxyl group, and yields a *diacetate*, melting at 120°, and a *dibenzoate*, melting at 149°. The benzoylmethylresorcinol is accompanied by *benzoylmethylresorcinol methyl ether*, $OMe{\cdot}C_6H_2MeBz{\cdot}OH$, which crystallises in rhombic tablets, melting at 125°. The *monacetate* melts at 86°.

A. H.

**Action of finely divided Silver on Ethylic Phenylbromacetate.** By CARL HELL and S. WEINZWEIG (*Ber.*, 1895, **28**, 2445—2454).—Phenylbromacetic bromide was prepared by the action of phosphorus pentabromide (2 mols.) on mandelic acid (1 mol.), and was then converted into the ethylic salt by dissolving it in ethylic alcohol. The authors find that the yield is just as good when one-half or even one-quarter of the theoretical quantity of pentabromide is used; this is due to the fact that the hydrogen bromide which is formed during the reaction also acts on the mandelic acid. The ethylic salt boils at 175° under a pressure of 25 mm., and small quantities may be distilled at ordinary atmospheric pressure without undergoing decomposition.

Finely divided silver acts on the ethylic salt at the ordinary temperature, but the action is greatly accelerated by heating the two together in an oil bath at 170—180°. No product of low boiling point could be isolated, but the ethereal extract yielded a mixture of $\alpha$- and $\beta$-ethylic diphenylsuccinates (compare Reimer, Abstr., 1882, 200), together with a small quantity of some oily ethylic salt which could not be obtained in a state of purity. Both $\alpha$- and $\beta$-salts, when hydrolysed with alcoholic potash, yield Reimer's $\alpha$-diphenylsuccinic acid, whereas when hydrolysed with hydrobromic acid they both yield the $\beta$-acid. The action of silver on ethylic phenylbromacetate is thus similar to its action on $\alpha$-brominated fatty acids generally, and we may suppose the two isomeric ethereal salts to be formed according to the two general reactions previously given (see this vol., i, 10). J. J. S.

**Reduction of Phenolcarboxylic acids.** By ALFRED EINHORN and JOHN S. LUMSDEN (*Annalen*, 1895, **286**, 257—277).—The authors' experiments show that whilst metaphenolcarboxylic acids are converted by reduction into $\gamma$-hydroxyhexamethylenecarboxylic acids, the ortho-derivatives generally yield dibasic acids of the pimelic series.

Pimelic acid is formed when salicylic acid is reduced with sodium and amylic alcohol (Abstr., 1894, i, 246). The quantity of this acid, which is formed on reducing ethylic salicylate or its ethyl ether, is extremely small, and probably arises from hydrolysis; the main product of the action consists of hexahydrobenzoic acid. By the action of sodium on ethylic pimelate moistened with alcohol, Dieckmann obtained ethylic $\beta$-ketohexamethylenecarboxylate (Abstr., 1894, i, 173), which is converted into ethylic hexahydrosalicylate on reduction. The authors have treated ethylic $\beta$-ketohexamethylenecarboxylate dissolved in amylic alcohol with sodium, and obtained pimelic acid. This acid is also formed when guaiacolcarboxylic acid is reduced.

*Phenylenaceticpropionic acid*, $COOH{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is obtained by reducing 2 : 3-hydroxynaphthoic acid (m. p. 216°) in the manner indicated; it is also formed when 2 : 1-hydroxynaphthoic acid (m. p. 156°) is reduced, a mixture of *ac*- and *ar*-tetrahydro-$\beta$-naphthol being produced at the same time. It crystallises from water in colourless, hexagonal prisms, and melts at 139°; it dissolves readily in ether and alcohol. The *calcium* and *barium* salts are anhydrous, the *silver* salt darkens slowly in daylight, and the *copper* salt is bright green; the *ethylic* salt is a viscous oil, which has an agreeable odour, and boils at 210—212° under a pressure of 40 mm. *Nitrophenylenaceticpropionic acid* crystallises from water in colourless, lustrous leaflets,and melts at 172°; it is sparingly soluble in cold water, but dissolves more readily in hot water, and is very soluble in alcohol and ether. The *calcium* salt is anhydrous, and the *silver* salt explodes readily when heated. When the calcium salt is submitted to dry distillation, β-ketotetrahydronaphthalene (Abstr., 1894, i, 419) is formed; if the latter is slowly added to boiling dilute nitric acid, phenylenediacetic acid is produced. M. O. F.

**Isomeric Bromocinnamic acids and Cinnamic acids.** By EMIL ERLENMEYER (*Annalen*, 1895, **287**, 1—25).—The author's experiments show that Glaser's α- and β-bromocinnamic acids are geometrically isomeric modifications of a bromocinnamic acid having the halogen in the α-position.

By the reduction of Glaser's β-bromocinnamic acid, in alcoholic solution, with zinc dust, an acid has been obtained which resembles Liebermann's isocinnamic acid in every respect except crystallographic form; it belongs to the monoclinic system, $a : b : c = 1·146 : 1 : 2·344$; $\beta = 79° 59'$. On other occasions, reduction of this acid gave rise to a mixture of cinnamic and allocinnamic acids, whilst the exclusive product of Glaser's α-bromocinnamic acid was ordinary cinnamic acid.

Transparent crystals of the new isocinnamic acid (m. p. 44°) rapidly become opaque, and then melt at 68°; this indicates the spontaneous transformation of the substance into allocinnamic acid. Aniline converts both modifications of isocinnamic acid into allocinnamic acid; and the aniline salt of isocinnamic acid (Liebermann, Abstr., 1890, 1417), when treated with alkali, yields allocinnamic acid. Treatment with concentrated sulphuric acid at 50° for 15 minutes converts allocinnamic acid and both modifications of isocinnamic acid into ordinary cinnamic acid.

When allocinnamic acid (0·5 gram) is dissolved in alcohol (5 c.c.), treated with zinc bromide (0·7 gram), and allowed to remain for several days at the ordinary temperature, dilution with 20 c.c. of water causes the separation of an oil which solidifies to crystals, consisting of isocinnamic acid. It seems probable, therefore, that when Glaser's β-bromocinnamic acid is reduced in alcoholic solution with zinc dust, a mixture of allocinnamic with ordinary cinnamic acid is first produced, the former being transformed into isocinnamic acid under the influence of zinc bromide.

Glaser has already shown that the α-bromocinnamic acid of low melting point is converted into the other modification when heated; the author's experiments prove that between the β-bromocinnamic acids the converse change takes place.

The author confirms the description already given by Michael and Browne of the treatment of phenylpropiolic acid with hydrogen bromide (compare also Abstr., 1892, 848).

The discovery of a second isocinnamic acid introduces a fourth isomeric phenylacrylic acid. An attempt is made to explain the relationship which exists between these four modifications.

M. O. F.

**Condensation of Glyoxylic acid with Amido-acids.** By CARL BOETTINGER (*Arch. Pharm.*, 1895, **233**, 199—209).—The amidobenzoic acids condense with glyoxylic acid in alcoholic solution to acids of the composition $COOH\cdot C_6H_4\cdot N{:}CH_2\cdot COOH$ These are yellow substances; they dissolve in alkaline carbonates, and form *di-silver salts:* the 1 : 2- and 1 : 3-compounds readily lose carbonic anhydride, but the 1 : 4-compound is more stable. No well-defined product was obtained by the action of glycocine on glyoxylic acid. The oxalates of the three amidobenzoic acids are described.

C. F. B.

**Benzenesulphonamides and Mixed Secondary Amines.** By OSCAR HINSBERG and A. STRUPLER (*Annalen*, 1895, **287**, 220—230; compare Abstr., 1893, i, 168). —*Diphenylsulphonethylenediamine*, $C_2H_4(NH\cdot SO_2Ph)_2$, is prepared by warming on the water bath a mixture of benzenesulphonamide, concentrated aqueous potash, and ethylenic bromide; it crystallises from alcohol in colourless needles, and melts at 168°.

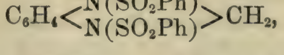
*Diphenylsulphonediethylethylenediamine* is obtained from the foregoing compound on treating it with potassium hydroxide and ethylic bromide or iodide; it separates from alcohol in minute crystals, and melts at 152·5°.

*Diethylethylenediamine*, $C_2H_4(NHEt)_2$, is formed when the sulphone derivative is heated with concentrated hydrochloric acid at 160° (Hofmann, *Jahresbericht*, 1859, 386); the hydrochloride crystallises in colourless needles.

*Diphenylsulphoneorthophenylenediamine*, $C_6H_4(NH\cdot SO_2Ph)_2$, is obtained on agitating orthophenylenediamine with benzenesulphonic chloride and excess of potash; it crystallises from glacial acetic acid in slender needles, and melts at 186°.

*Tetraphenyldisulphoneorthophenylenediamine*, $C_6H_4[N(SO_2Ph)_2]_2$, is obtained from phenylsulphoneorthophenylenediamine (Lellmann, *Annalen*, **221**, 17) by the protracted action of benzenesulphochloride and soda; it dissolves with difficulty in ordinary solvents, and melts at 150—151°.

*Diphenylsulphonemethyleneorthophenylenediamine*,



$$C_6H_4{<}\begin{matrix}N(SO_2Ph)\\N(SO_2Ph)\end{matrix}{>}CH_2,$$

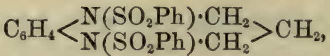
is prepared by adding methylenic iodide to a solution of diphenylsulphonephenylenediamine and sodium ethoxide in alcohol, and heating the mixture until it is neutral; it melts at 147—148°, and is converted by hydrochloric acid at 160° into phenylic bisulphide.

*Diphenylsulphonethyleneorthophenylenediamine* separates from glacial acetic acid in colourless crystals, and melts at 180°.

*Ethylenephenylenediamine* (tetrahydroquinoxaline) is obtained from the foregoing derivative by treatment with concentrated hydrochloric acid at 160—170° (compare Merz and Ris, Abstr., 1887, 722).

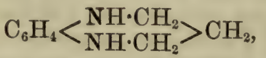
The *dinitroso*-derivative crystallises in minute, yellow needles, and melts and decomposes at 168°.

*Diphenylsulphonetrimethylenephenylenediamine*,



$$C_6H_4{<}\begin{matrix}N(SO_2Ph)\cdot CH_2\\ N(SO_2Ph)\cdot CH_2\end{matrix}{>}CH_2,$$

separates from glacial acetic acid in colourless crystals, and melts at 204—205°.

*Trimethylenephenylenediamine*,  $C_6H_4{<}\begin{matrix}NH\cdot CH_2\\ NH\cdot CH_2\end{matrix}{>}CH_2$, is obtained from the foregoing derivative by treatment with concentrated hydrochloric acid at 170°; it melts at 102°, boils at 290—300°, and reduces an ammoniacal silver solution when heated with it. Ferric chloride develops a violet-red colour with the base. The *dinitroso*-derivative melts at 120°.

*Diphenylsulphonemetaphenylenediamine* crystallises from alcohol or glacial acetic acid, and melts at 194°. When the sodium derivative is treated in alcoholic solution with ethylenic bromide (1 mol.), a *compound* of the formula $C_{20}H_{18}N_2S_2O_4$ is formed; it melts at 190—195°. M. O. F.

**Parabromanilinesulphonic acids: A New Method of Preparing Benzoicsulphinide.** By HANS KREIS (*Annalen*, 1895, **286**, 377—388).—*Parabromanilinemetasulphonic acid* [Br : $HSO_3$ : $NH_2$ = 1 : 2 : 4] is prepared by dissolving parabromacetanilide (30 grams) in fuming sulphuric acid (200 grams) containing 15 per cent. of sulphuric anhydride, and heating the liquid at 140—150° in an oil bath; effervescence takes place, and when this has ceased, the liquid is poured on to 600 grams of ice. The sulphonic acid crystallises from water in slender, white needles containing the solvent, which is eliminated on exposure to air; the *barium* salt is anhydrous. When parabromanilinemetasulphonic acid is reduced with caustic soda and zinc dust, anilinemetasulphonic acid is formed.

Parabromanilineorthosulphonic acid is obtained by heating parabromacetanilide (20 grams) with sulphuric acid (10 grams) at 170—180° for one hour; it crystallises in anhydrous leaflets, and in needles containing $1H_2O$.

*Parabromocyanobenzeneorthosulphonic acid* is obtained from the foregoing substance by means of Sandmeyer's reaction; the *sodium* and *potassium* salts crystallise in colourless, silky needles, and contain $1\frac{1}{2}H_2O$. The *sulphonic chloride* separates from a mixture of benzene and petroleum in lustrous crystals, and melts at 90°, and the *sulphonamide* is a white powder which melts above 250°; it crystallises from pyridine in leaflets which contain the solvent.

Parabromobenzoicsulphinide is obtained by heating the sulphonamide with aqueous caustic soda; it melts at 227·5° (compare Remsen and Bayley, *Ber.*, 1886, **19**, 835).

Anilineorthosulphonic acid is obtained by eliminating the bromine from parabromanilineorthosulphonic acid by means of caustic soda and zinc dust; from this substance the author has prepared several compounds which have been already described (Abstr., 1893, i, 715), and records the production of benzoicsulphinide by heating orthocyanobenzenesulphonamide dissolved in 25 parts of water with one molecular proportion of sodium hydroxide. M. O. F.

**Formation of Indigo by the Action of Sunlight.** By Carl Engler and K. Dorant (*Ber.*, 1895, **28**, 2497—2501; compare *Ber.*, **3**, 885, and Abstr.,1895, i, 231).—An alcoholic solution of orthonitroacetophenone readily condenses with benzaldehyde, in the presence of dilute sodium hydroxide solution, to form *benzylideneorthonitroacetophenone*, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CHPh$; this crystallises in long, colourless, silky needles, melts at 124°, and forms a *hydrazone* which melts at 146—147°. When the ketone is spread on a shallow plate and exposed to bright sunlight, it is rapidly decomposed into indigo and benzoic acid, owing to the oxidising action of the nitro-group on another part of the molecule. No action takes place in the dark, and the rate at which the ketone is converted into indigo depends on the nature of the rays, being greatest when a blue glass plate is interposed between the substance and the sun. Similar intramolecular oxidations have been previously observed by Baeyer (Abstr., 1881, 274; 1883, 341) and by Friedlaender (Abstr., 1895, i, 543).

*Benzylideneorthoamidoacetophenone* is formed when the nitro-ketone is reduced with stannous chloride. It crystallises in prisms which melt at 147°, and its *salts* are deep red; the *acetyl* derivative melts at 165°, the *hydrazone* at 154°, and a *bromo-derivative* at 159—160°. Ferric chloride oxidises the amido-ketone to a substance which melts at 214—216°; other products are also formed. When the nitroketone is reduced with zinc dust and boiling water, a substance melting at 68° is formed together with the amido-compound. This product is being further examined, as it does not give the reaction of the expected hydroxylamine derivative. J. J. S.

**Sulphonephthaleïns.** By John White, jun. (*Amer. Chem. J.*, 1895, **17**, 545—556; compare Abstr., 1889, 710).—When sulphonefluoresceïn is treated with bromine, a dibromo-substitution product is chiefly formed, and with phosphorus pentachloride a tetrachloroderivative, which appears to be produced by the displacement of the two hydroxyl groups and the anhydride oxygen in the sulphonefluoresceïn.

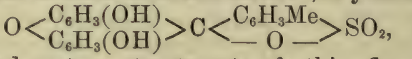
It is not possible to prepare sulphonefluoresceïn by the action of resorcinol on orthosulphobenzoic acid, but when an action between these compounds occurs, either four or six residues of resorcinol enter into combination according to the conditions of experimentation.

No pure compounds are described in the paper. A. G. B.

**Sulphonephthaleïns from Orthosulphoparatoluic acid.** By Walter Jones (*Amer. Chem. J.*, 1895, **17**, 556—569).—*Ammonium paramethyldihydroxybenzoylbenzenesulphonate*,

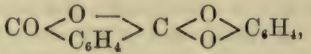
$$C_6H_3(OH)_2{\cdot}CO{\cdot}C_6H_3Me{\cdot}SO_3NH_4,$$

is prepared by heating ammonium hydrogen orthosulphoparatoluate (Abstr., 1891, 1228) with resorcinol; it forms colourless crystals, and its aqueous solution yields an insoluble *basic lead salt*, with $12H_2O$, when boiled with minium; the corresponding *acid* is obtained by decomposing the lead salt with hydrogen sulphide, and forms colourless crystals, with $4H_2O$. The *barium* salt $(C_{13}H_{11}SO_6)_2Ba + 5H_2O$, the normal *lead* salt, with $7H_2O$, the *calcium* salt, with $6H_2O$, the *zinc* salt, with $xH_2O$, and the *silver* salt, with $2H_2O$, are described.

Attempts to substitute other acid radicles for the phenolic hydroxyl groups in paramethyldihydroxybenzoylbenzenesulphonic acid proved unsuccessful. When the acid is heated at 170°, it yields *paramethylsulphonefluoresceïn*,  $O<\genfrac{}{}{0pt}{}{C_6H_3(OH)}{C_6H_3(OH)}>C<\genfrac{}{}{0pt}{}{C_6H_3Me}{—O—}>SO_2$, orthosulphoparatoluic acid, and water; treatment of this fluoresceïn with phosphorus pentachloride, produces a *tetrachloro*-derivative, and treatment with excess of bromine, produces a dibromo-substitution product which fluoresces like eosin.

Two other sulphonephthaleïns can be derived from orthosulphoparatoluic acid, by treating it with resorcinol; one containing four and the other six resorcinol residues. A. G. B.

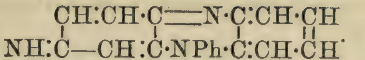
**Allofluoresceïn.** By BRONISLAW PAWLEWSKI (*Ber.*, 1895, **28**, 2360—2362; compare Abstr., 1895, i, 219).—*Allofluoresceïn*,



$$CO<\genfrac{}{}{0pt}{}{O\ —}{C_6H_4}>C<\genfrac{}{}{0pt}{}{O}{O}>C_6H_4,$$

is obtained by heating resorcinol with phthalic chloride alone or in solution, on the water bath; the red or yellow product is then treated with acetic anhydride for several hours at 150—170°, and, after evaporating the liquid, the residue is repeatedly extracted with glacial acetic acid and with alcohol. The colourless, amorphous substance melts at 140°, and is almost insoluble in the majority of organic solvents; it dissolves to some extent in boiling glacial acetic acid, and to a greater degree in acetic anhydride and ethylic acetate, separating from solution in the amorphous state. The freshly prepared substance dissolves readily in alkalis and alkali carbonates, the liquid exhibiting strong fluorescence; the dried or fused substance, however, dissolves in concentrated alkalis with great difficulty. The fluorescence of solutions in ammonia or barium hydroxide is green.

The paper contains a detailed comparison of allofluoresceïn with the ordinary modification. M. O. F.

**Relation of the Indulines to the Safranines.** By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1895, **28**, 2283—2289).—Phenosafranine belongs to the same group of compounds as the mauveïnes, indulines, and indazines. On treatment with alkalis, it yields safranol, or hydroxyaposafranone, which only contains one hydroxyl-group, so that phenosafranine must itself be free from water, at all events at 100°. Aposafranine, which is obtained from phenosafranine by the removal of the amido-group, therefore, is to be looked on as the simplest meso-phenyl derivative of the series, corresponding with rosinduline, its formula being  $\begin{array}{l}\mathrm{CH{:}CH{\cdot}C{=\!=\!=}N{\cdot}C{:}CH{\cdot}CH} \\ \mathrm{NH{:}C{-}CH{:}C{\cdot}NPh{\cdot}C{:}CH{\cdot}CH}\end{array}$. The facts, which, previously, were apparently at variance with this view, have now been more accurately investigated. The free base itself is free from water, like phenosafranine (Abstr., 1895, i, 608), and the *benzoyl* derivative is also anhydrous. This substance crystallises from benzene in dark violet plates, which contain 1 mol. of benzene; it is strongly basic, and forms yellow salts. The relation between aposafranine and the simplest benzene-induline, appears to be precisely similar to that between aposafranone and the simplest benzeneindone. When aposafranone is heated with aniline and aniline hydrochloride, it is converted into the substance previously termed benzeneindone (*Annalen*, 1884, **226**, 254), and formulated as $C_{18}H_{12}N_2O$. The formation of this substance from aposafranone now shows that its true formula must be $C_{24}H_{17}N_3O$, and it is, therefore, *anilidoaposafranone*. When it is boiled with 75 per cent. sulphuric acid, it is converted into *hydroxyaposafranone*, $C_{18}H_{14}N_2O_2$, which was previously described as benzeneindonehydrate. Hydroxyaposafranone is also formed when aposafranone is boiled with alcoholic potash. Anilidoaposafranone may be reconverted into aposafranone by boiling with 60 per cent. acetic acid and zinc dust. In the same way, the simplest induline derived from aposafranine, which is known as anilidoaposafranine (Kehrmann) may be reconverted into aposafranine.

Phenylinduline, which is derived from benzeneindone by the displacement of a single atom of hydrogen by the anil-group, must now receive the formula $C_{30}H_{22}N_4$, instead of that previously assigned to it, and all the indulines must be classed as anilidosafranines, their formulæ being altered in accordance with this relationship.

A. H.

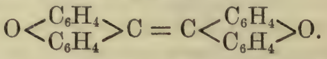
**Action of Alkalis on Paranitrotoluenesulphonic acid.** By Otto Fischer and Eduard Hepp (*Ber.*, 1895, **28**, 2281—2283; compare Abstr., 1893, i, 697). The authors, in reply to Bender's criticism (Abstr., 1895, i, 287), maintain the accuracy of the results obtained by them in the reduction of paranitrosostilbenedisulphonic acid by means of ferrous sulphate, and its oxidation by chromic acid, new experiments having given the same results as the ones previously quoted.

A. H.

**Synthesis of Bidiphenyl and its Identification as Benzerythrene.** By Arthur A. Noyes and Rolfe M. Ellis (*Amer. Chem. J.*, 1895, **17**, 620—622).—*Parabidiphenyl*, $PhC_6H_4{\cdot}C_6H_4Ph$, was prepared from parabromodiphenyl by boiling an ethereal solution of it with sodium; the solid matter was separated, washed with water and benzene, and sublimed. It forms large, crystalline laminæ, melts at 317°, and distils at 428° (18 mm. pressure); it is insoluble in boiling alcohol, ether, chloroform, and carbon bisulphide; boiling benzene dissolves it sparingly. The compound termed benzerythrene, $C_{24}H_{18}$, by Schmidt and Schultz (*Annalen*, 1880, **203**, 18), and obtained by the action of heat on benzene, melted at 308°, and was insoluble in alcohol, but slightly soluble in boiling benzene. The

authors conclude that benzerythrene is identical with parabidiphenyl.
A. G. B.

**Reduction Product of Xanthone.** By G. GURGENJANZ and STANISLAUS VON KOSTANECKI (*Ber.*, 1895, **28**, 2310—2311).—When xanthone is boiled with acetic acid and zinc dust, it is converted into dixanthylene (tetraphenyleneethylenedioxide),

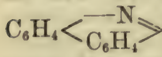


$$O{<}{C_6H_4 \atop C_6H_4}{>}C = C{<}{C_6H_4 \atop C_6H_4}{>}O.$$

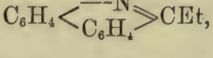
This crystallises from benzene in long, thick, almost white needles, which melt at 315°. The solution in benzene has a bluish-green fluorescence. 4 : 5-Dimethylxanthone is converted by similar treatment into 4 : 5 : 4′ : 5′-*tetramethyldixanthylene*, which does not melt below 360°. 2 : 7-Dimethylxanthone yields 2 : 7 : 2′ : 7′-*tetramethylxanthylene* which sublimes without decomposition at 275—277°.
A. H.

**Benzylidene-β-dinaphthylic Oxide.** By E. MERCK (*Chem. Centr.*, 1895, i, 431; from *Ber. ü. d. Jahr.*, 1894, 21—22).—The residue obtained during the preparation of benzoyl-β-naphthol contains benzylidene-β-dinaphthyl oxide (m. p. 188—191°); it must have been formed from benzaldehyde or benzylidene chloride contained in the benzoic chloride employed.
J. B. T.

**Synthesis of Phenanthridine.** By AMÉ PICTET and A. HUBERT (*Chem. Centr.*, 1895, 432—433; from *Arch. sci. phys. Genève*, 1894, **32**, 493—504).—The method employed consists in the condensation, by means of zinc chloride, of acidyl orthoamidodiphenyl derivatives, $RNH{\cdot}C_6H_4Ph$. Orthoamidodiphenyl is most readily prepared by Graebe and Rateanu's method (Abstr., 1894, i, 529).

2-*Formylamidodiphenyl*, $COH{\cdot}NH{\cdot}C_6H_4Ph$, crystallises in colourless needles, melts at 75°, and, when heated with zinc chloride (5 parts) at 280—300°, yields phenanthridine. *Mesomethylphenanthridine*,  $C_6H_4{<}{—N \atop C_6H_4}{\gg}CMe$, is formed in a similar manner at 320° from acetylamidodiphenyl; it crystallises in small, colourless needles, and melts at 85°. The *hydrochloride* and *mercurochloride* are colourless, and melt at 285° and 247° respectively. The *picrate* and *methiodide* are yellow, and melt at 233° and 263° respectively. The *platinochloride* $(C_{14}H_{12}N)_2PtCl_6 + 2H_2O$ (m. p. 272°) is flesh-coloured; the *dichromate* is orange-yellow, and darkens at 150°; the *aurochloride* (m. p. 163—164°) is pale yellow. All these derivatives crystallise in needles.

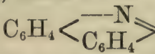
2-*Propionylamidodiphenyl* crystallises in colourless, lustrous needles; it melts at 65°, and yields *mesoethylphenanthridine*,



$$C_6H_4{<}{—N \atop C_6H_4}{\gg}CEt,$$

which is deposited from light petroleum in small, colourless needles melting at 54—55°. The following derivatives crystallise in needles.

The *hydrochloride* and *mercurochloride*, melting at 205° and 214° respectively; the *dichromate* is golden yellow; the *picrate* is pale yellow, slowly decomposes when heated, and melts at about 210°; the *platinochloride*, $(C_{15}H_{13}N)_2,H_2PtCl_6 + 2H_2O$, and the *aurochloride*, are yellow, and melt at 241—242° and 149° respectively.

2-*Benzoylamidodiphenyl*, $NHBz{\cdot}C_6H_4Ph$, crystallises in pearly, lustrous plates, melts at 85—86°, and at 300—360° yields *mesophenylphenanthridine*,  $C_6H_4<\begin{matrix}—N\\C_6H_4\end{matrix}>CPh$, which is also formed by heating a mixture of amidodiphenyl, benzoic acid, and zinc chloride; it crystallises in iridescent, transparent, quadratic plates, melts at 109°, boils above 360°, is a feeble base, and dissolves in dilute mineral acids with a violet fluorescence. Its salts are only stable in presence of acid; they are decomposed by water. The *hydrochloride*,

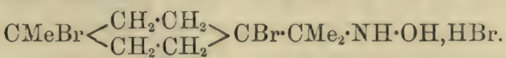
$$C_{19}H_{13}N,HCl + H_2O,$$

crystallises in yellow prisms melting at 95—96°; the anhydrous compound forms pale yellow needles, and melts at 220°. The *platinochloride* crystallises with $2H_2O$ in yellow needles, and decomposes at about 300°. *Orthodiphenylurethane*, $C_6H_4Ph{\cdot}NH{\cdot}COOEt$, prepared from orthamidodiphenyl and ethylic chlorocarbonate crystallises in colourless needles, melts at 186°, and, when heated with zinc chloride, yields phenanthridone. J. B. T.

**Orientation in the Terpene Series.** By ADOLF VON BAEYER and FRITZ BLAU (*Ber.*, 1895, **28**, 2289—2297; compare Abstr., 1894, i, 252).—1-*Bromo*-$\Delta^{4\cdot8}$-*terpene* is formed when Wallach's terpene tribromide is dissolved in a mixture of alcohol and ether, and treated with zinc-dust; it forms compact rhombic prisms, melting at 34—35°. Hydrogen bromide converts it into dipentene dihydrobromide, along with an oily substance. When bromoterpene is treated with sodium nitrite and hydrobromic acid, the *nitrosobromide* is formed in blue crystals, which melt at 44°, but could not be obtained quite pure.

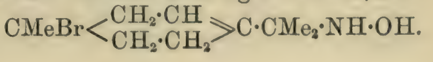
$\Delta^{4\cdot8}$-Terpenol acetate also yields a *nitrosobromide*, which crystallises in blue needles, and melts at 81—82°.

The two nitroso-bromides just described yield the same product when they are treated with a solution of hydrogen bromide in acetic acid, bromine being in both cases set free. This product crystallises in thin, quadratic plates, which melt at 182—184°, its constitution being most probably expressed by the formula,



$$CMeBr<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>CBr{\cdot}CMe_2{\cdot}NH{\cdot}OH,HBr.$$

It reduces silver salts and Fehling's solution.

When this substance is dissolved in water, and potash or ammonia added, 2 mols. of hydrogen bromide are removed, and a base, $C_{10}H_{18}NOBr$, is obtained, which crystallises in indefinite forms, and melts at 100—102°. This base also reduces Fehling's solution, and probably has the constitution,  $CMeBr<\begin{matrix}CH_2{\cdot}CH\\CH_2{\cdot}CH_2\end{matrix}>C{\cdot}CMe_2{\cdot}NH{\cdot}OH.$

Nitrous acid converts it into a nitroso-compound, $C_{10}H_{17}BrN_2O_2$, which crystallises in serrated, rhombic tablets, melting at 138—139°. This substance may be obtained by a similar series of reactions from each of the three compounds, the nitrosobromide of bromoterpene, the nitrosobromide of terpenol, and the nitrosochloride of terpenol acetate, a fact which confirms the formulæ proposed.

The product of the action of hydrogen bromide on the nitrosochloride of terpenol acetate has the formula, $C_{10}H_{20}NOClBr_2$, and crystallises in almost rectangular tablets melting at 179—180°.

The hydroxylamine derivative, $C_{10}H_{18}NOBr$, which is formed from the nitrosobromide by the action of hydrogen bromide, is converted by the action of bromine into the original nitrosobromide, so that the action is a reversible one.

*Trihydroxyterpane*, $C_{10}H_{20}O_3$, is formed by the action of dilute potassium permanganate solution on $\Delta^{4\cdot 8}$-terpenol. It forms crystals which contain 1 mol. water, and melts at 95—96°. The anhydrous substance melts at 110—112°, and boils at 200° (pressure = 20 mm.) almost without decomposition. Hydrobromic acid converts it into Wallach's tribromide.

A considerable amount of a substance which melts at 127—128°, and has the formula of dipentene tetrabromide, is formed during the preparation of the tribromide from dipentene dihydrobromide.

A. H.

**From Pinene to Carvacrol.** By JOHN L. MEAD and EDWARD KREMERS (*Amer. Chem. J.*, 1895, **17**, 607—611).—Urban and Kremers have already shown that "nitrosopinene" is really an oxime, and that it yields an oil, $C_{10}H_{14}O$, on hydrolysis (Abstr., 1894, i, 468). It is now shown that this oil is carvacrol (compare von Baeyer, Abstr., 1895, i, 379).

A. G. B.

**Ethereal Oils.** By EDUARD GILDEMEISTER (*Arch. Pharm.*, 1895, **233**, 174—189).—The oil expressed from the rind of sweet limes (*Citrus Limetta Risso*), growing in South Europe, was found to contain limonene with possibly a little phellandrene; also, in smaller amount, linalyl acetate, together with a little linalöol; it thus resembles oil of bergamot, which contains dipentene in addition. The sample examined was brownish-yellow, had the sp. gr. = 0·872 at 15°, and $[\alpha]_D = +66° 52'$. Linalöol was identified by oxidising it with chromic mixture to geranaldehyde, and converting this, by Doebner's method (Abstr., 1894, i, 261), into citryl-β-naphthocinchoninic acid, melting at 197°.

Four samples of oil of origanum from Smyrna were examined; their exact botanical origin was unknown, perhaps they were obtained from *Origanum smyrnaicum.* The sp. gr. was 0·916—0·932 at 15°; the rotation in a length of 100 mm. −7° 52′ and −8° 44′ in two of the samples; the percentage of phenols (by shaking 10 c.c. of the oil with 50 c.c. of 5 per cent. soda, and noting the volume of the residual oil) 32·47; all the samples dissolved in 2½ parts of alcohol of 70 per cent. strength by volume. The oil was found to consist mainly of linalöol; cymene is also present, and possibly an "olefinic terpene" (compare Semmler, Abstr., 1891, 655, and Chapman, Trans., 1895, 58); the phenol present is mainly carvacrol, but there is a small quantity of a phenol that gives a violet colour with ferric chloride. Carvacrol was identified by means of its phenylic cyanate derivative (Goldschmidt, Abstr., 1893, i, 723); cymene by oxidising it with potassium dichromate and dilute sulphuric acid on the water bath to hydroxypropylbenzoic acid, melting at 156—158°, and converting this by boiling with fuming hydrochloric acid into isopropenylbenzoic acid, melting at 255 – 260° (Wallach, *Annalen*, **264**, 10).

C. F. B.

**Oil of Lignaloes.** By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1895, **121**, 168—170).—Oil of lignaloes contains, in 1000 parts, 1 part each of a bivalent terpene, a quadrivalent terpene, and methylheptenone, 20 parts of licarhodol, 30 parts of a sesquiterpene, and 900 parts of licareol. The sesquiterpene, $C_{15}H_{24}$, boils at 135—136° under a pressure of 10 mm., has a faint, pleasant odour, and combines with 4 atoms of bromine; its proportion varies considerably in different specimens of the oil. The methylheptenone is always present in the oil, and is identical with the methylheptenone obtained by Wallach by the decomposition of cinoleïc anhydride; it is isomeric with that found in oil of lemon-grass (Abstr., 1894, i, 401), and, when heated with zinc chloride, is converted into dihydrometaxylene, $C_8H_{12}$, boiling at 134°. A small part of the licareol is present in the oil in combination with acetic acid and higher acids of the same series.

C. H. B.

**Oxidation of Inactive Campholenic acid.** By AUGUSTE BÉHAL (*Compt. rend.*, 1895, **121**, 213—216).—When oxidised with nitric acid of sp. gr. 1·27, inactive campholenic acid yields hydroxycamphoronic acid, melting at 167—168°, isobutyric acid, and two dibasic acids, $C_7H_{12}O_4$ and $C_6H_{12}O_4$.

The *acid* $C_7H_{12}O_4$ is very soluble in water, benzene, or ether, crystallises from a mixture of benzene and light petroleum, and melts at 83·5°. Its calcium salt, $C_7H_{10}O_4Ca + 3H_2O$, crystallises in flattened, orthorhombic prisms. The *anhydride* melts at 38·5°, and boils at 270°; in presence of benzene, it reacts with aniline, and yields the compound $C_6H_{11}O_2{\cdot}CO{\cdot}NHPh$, which crystallises from dilute alcohol, melts at 146°, and, when distilled with water, is converted into the imido-compound, $C_5H_{10}{<}\substack{CO\\CO}{>}NPh$, which melts at 121·5°. The acid $C_7H_{12}O_4$ seems to be a glutaric derivative; its *ethylic* salt boils at 235—238°.

The *acid* $C_6H_{10}O_4$ melts at 144°, and is very soluble in water; its *ethylic* salt boils at about 230°, and its *anhydride* at about 220°; the *phenylamido*-derivative melts at 185°, and the *phenylimido*-derivative at 86°.

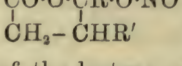
C. H. B.

**Action of Nitric Peroxide on Campholenic acid.** By AUGUSTE BÉHAL and VICTOR BLAISE (*Compt. rend.*, 1895, **121**, 256—259).—When nitric peroxide is passed over inactive campholenic acid until the latter has absorbed a molecular proportion of it, a blue liquid is formed, and when this is treated with a cold saturated solution of potassium hydrogen carbonate, a blue oil remains undissolved and soon solidifies. When this product is dried and crystallised from alcohol of 80°, *ceruleonitrosocampholenolide*, $C_{10}H_{15}NO_3$, is obtained in thin lamellæ, which melt at 134·5°, and have a blue colour similar to that of copper sulphate. It has a neutral reaction, and is insoluble in alkali hydrogen carbonates. If an alcoholic solution is exposed to diffused light for some days, a white, amorphous modification, *leuconitrosocamplolenolide*, separates. Unlike the blue compound, it is insoluble in ordinary organic solvents, but when heated with them, or alone, it is reconverted into the blue modification, of which it seems to be a polymeride, although its molecular weight could not be determined.

Ceruleonitrosocampholenolide, when treated with alcoholic potash, yields a red azo- or azoxy-derivative, which is decolorised by sodium amalgam, and regenerated by oxidation with mercuric oxide. The product of reduction by the amalgam reduces Fehling's solution in the cold. When boiled with tin and acetic acid, the ceruleonitrosocampholenolide yields an unsaturated lactone, which melts at 31·5°, and an amine acetate, which melts at 97°.

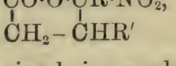
Excess of nitric peroxide converts campholenic acid into the compound $C_{10}H_{15}NO_4$, which melts at 175°, and has been described by several previous observers as nitrocampholenic acid. It has, however, no acid function; it is neutral to litmus, and does not decompose alkali hydrogen carbonates. When boiled with potassium hydrogen carbonate, it yields didehydrocampholenolide, $C_{10}H_{14}O_2$, a crystalline compound, which melts at 31·5°, and boils at 193° under a pressure of 17 mm. When boiled with alkali hydroxides, it is converted into dihydroketocampholenic acid, $C_{10}H_{16}O_3$, which crystallises from benzene or dilute alcohol in prismatic needles, and melts at 126° if heated rapidly, or at 112° if kept at this temperature for some time. It begins to change into a lactone above 100°, and at 150°, it yields the original lactone. The acetate of the amine, obtained by reduction of so-called nitrocampholenic acid, crystallises well from absolute alcohol, and melts at 97°.

It would seem that the so-called nitrocampholenic acid is really a nitrocampholenolide; it has a lactonic function, and the $NO_2$ group seems to exist in two forms, which are probably tautomeric,



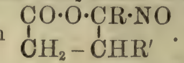
$$\begin{array}{l} CO\cdot O\cdot CR\cdot O\cdot NO \\ CH_2-CHR' \end{array}$$

and



$$\begin{array}{l} CO\cdot O\cdot CR\cdot NO_2, \\ CH_2-CHR' \end{array}$$

the constitution of the lactone and amine being analogous, although the position of the ethylene linking is somewhat uncertain. The ketonic acid probably has the constitution $COOH\cdot CH_2\cdot CHR'\cdot COR$, and ceruleonitrosocampholenolide the constitution



$$\begin{array}{l} CO\cdot O\cdot CR\cdot NO \\ CH_2-CHR' \end{array}.$$

C. H. B.

**Campholic acid.** By Guerbet (*Ann. Chim. Phys.*, 1895, [7], 4, 239—365).—The greater part of the work contained in this paper has previously been published (compare Abstr., 1894, i, 254; 1895, i, 61, 240, 295, and 383. Also Errara, Abstr., 1892, 1345; 1893, i, 108). It is shown that campholic acid is practically not acted on by hydrochloric or hydrobromic acid at 200°.

Campholene hydriodide (Abstr., 1894, i, 254) melts at about 52° when rapidly heated.

The nitrosochloride (Béhal, Abstr., 1895, i, 240) forms an indigo-blue crystalline mass, and melts at 25° when rapidly heated. The author thinks most of his results support the hydroxyketone formula of campholic acid suggested by Friedel. J. J. S.

**Gedanite, Succinite, &c.** By OTTO HELM (*Arch. Pharm.*, 1895, **233**, 191—199; compare Tschirch and Aweng, Abstr., 1895, i, 384).—Gedanite does not contain free succinic acid, although Aweng states that it does; the dealer had, doubtless, sent him as gedanite what was really a specimen of succinite (ordinary amber). Gedanite further differs from succinite in that it contains 2—3 per cent. more carbon and about as much less oxygen; it contains some sulphur, but less than succinite does. A much larger proportion of gedanite dissolves in various solvents than is the case with succinite; it is even entirely soluble in linseed oil. There is a variety of succinite known as "soft" or "friable amber" ("*mürber Succinit*"), which is intermediate in its properties between gedanite and true succinite. C. F. B.

**Opoponax from Burseraceæ.** By A. BAUR (*Arch. Pharm.*, **233**, 209—252).—The substance once known by this name had a rather unpleasant odour, and was probably derived from a Persian member of the *Umbelliferæ*. The substance now known as opoponax contains a pleasant smelling ethereal oil, which is used as a perfume; the samples examined by the author contained plant fragments which showed them to be derived from some member of the genus *Balsamodendron*, order *Burseraceæ*—probably from *B. Kafal*. It contains 19 parts per cent. of resin, 6·5 of ethereal oil, and 70 of gum, besides plant fragments. The resin contains *α-panax-resen*, $C_{32}H_{54}O_4$, soluble in light petroleum; *β-panax-resen*, $C_{32}H_{52}O_5$, insoluble in light petroleum, but soluble in ether; and *panaresinotannol*, $C_{34}H_{50}O_8$, insoluble in light petroleum, and only slightly soluble in ether, but soluble in alcohol, and also, unlike the preceding two, in alkalis. These are yellowish-brown substances, which can be powdered when cold, but are plastic when warm; it was not found possible to hydrolyse them, nor could well-characterised substances be obtained from them in any way. The ethereal oil possibly contained a terpene; the portion of higher boiling point yielded, when hydrolysed, an *alcohol*, $C_{56}H_{96}O$, boiling at 250—255° (uncorr.), and, apparently, a fatty acid (? butyric). This oil is obtained from the drug by treating it with superheated steam; the residue then contains a new substance which is not present in the original drug. This is *chironol*, $C_{28}H_{48}O$, a white, crystallised substance, soluble in ether and hot alcohol, and melting at 176° (uncorr.); it yields crystallised *monacetyl* and *monobenzoyl derivatives*, melting respectively at 196° and 186° (uncorr.), and is oxidised by permanganate in hot acetic acid solution to *chironolic acid*, $C_{28}H_{48}O_4$, a white, amorphous substance, which melts at 100—108°, dissolves in alkalis, but not in water; and, in alcoholic solution, reddens litmus paper. Opoponax also contains an alkaloïd, which could not, however, be obtained crystallised. Unlike the oils from Persian *Umbelliferæ*, it contains no umbelliferone and no sulphur.

Mecca balsam also contains resins resembling those of opoponax in character; resins, that is, that cannot be hydrolysed, and so cannot have the constitution of ethereal salts. To "indifferent" resins, which have the character neither of ethereal salts, acids, nor alcohols, Tschirch has given the name of "resens." C. F. B.

**Sagapen.** By M. HOHENADEL (*Arch. Pharm.*, 1895, **233**, 259—286).—This substance is obtained from the stems and fruits of a Persian species of *Ferula*, order *Umbelliferæ*, as was shown by an examination of the plant fragments contained in the drug. The sample examined by the author contained resin, 56·8; ethereal oil, 5·8; water, 3·5; gum, 23·3; and impurities 10·6 per cent. The purified resin is yellowish-brown, and is brittle when cold, plastic when warm, melting at 74—76°; it yields a sublimate of umbelliferone when heated, and, when hydrolysed by boiling with sulphuric acid, it is decomposed into umbelliferone and sagaresinotannol, of which two substances it is the ethereal salt. *Sagaresinotannol*, $C_{24}H_{28}O_5$, is a brown substance soluble in alkalis, and yielding a precipitate with ferric chloride; it yields *monacetyl* and *monobenzoyl derivatives*, and is oxidised by nitric acid to styphnic acid (trinitroresorcinol). The 56·8 parts of purified resin contains 40 of sagaresinostannol, 15·7 of combined, and 0·11—0·15 of free umbelliferone. The ethereal oil contains 9·7 per cent. of sulphur, and probably contains an ethereal salt of valeric acid; the bluish fraction boiling at 210—270° was found to resemble, as regards its absorption spectrum, the similar bluish or greenish fractions, of much the same boiling point, obtained from the oils of galbanum, asafœtida, chamomile, valerian, Japanese valerian, millefoil, absinth, and *Inula Helenium*. The substance contained in it, "azulene," is not, however, present in the original oil, but is formed during the process of fractionation. C. F. B.

**Digitalin.** By HEINRICH KILIANI (*Arch. Pharm.*, 1895, 299—310).—"The glucosides obtained from the seeds of *Digitalis purpurea* consist, to the extent of at least one-half, of digitonin, which can easily be obtained crystallised" by digesting *Digitalinum pur. pulv. germanic.* with four times its weight of 85 per cent. alcohol. "They contain *Digitalinum verum* (digitalin) as the essential constituent, to which alone their action on the heart is due; the existence of 'digitaleïn' is, to say the least, doubtful. In addition they contain a well-crystallised organic compound containing calcium and potassium. Digitonin and *Digitalinum verum* are both, when pure, very sparingly soluble in water. The ready solubility of the mixture of glucosides (*Digitalinum pur. pulv.*) is due solely to the presence of resinous amorphous substances, in addition. Digitogenin was not detected in Merck's samples. It is certain that the crystals, which Schmiedeberg described as digitin, were nothing but digitonin."

The author has worked out the following method, by means of which *Digitalinum verum* is now prepared on the large scale:—

"One part by weight of *Digitalinum pur. pulv.* is dissolved, by means of a gentle heat, in four of 95 per cent. alcohol. The cold solution is stirred or shaken, and five parts of ether (sp. gr. 0·72) are, meanwhile, added, and the whole allowed to remain for 24 hours in a closed vessel. The alcohol-ethereal solution is then drawn off, weighed or measured, and the weight of solid matter in it (= A) determined by evaporating a portion. The ether and most of the alcohol are then distilled off under reduced pressure until the weight of the residual solution is 1·6 A; 2·4 A parts of water are then added, and the mixture is allowed to stand for 24 hours in a closed vessel. The crude digitalin which has separated is now brought on to a filter, allowed to drain without suction being applied, washed with 10 per cent. alcohol, and, finally, with water, and dried on porous plates or in a vacuum. The dry substance is then 'recrystallised' from 95 per cent. alcohol, with the addition of animal charcoal." It is thus obtained in white granules. C. F. B.

**β-Digitoxin.** By Heinrich Kiliani (*Arch. Pharm.*, 1895, **233**, 311—320).—The leaves of *Digitalis purpurea* contain neither digitonin nor digitalin, but a new glucoside, *β-digitoxin*, $C_{28}H_{46}O_{10} + 5H_2O$, can be obtained from them by successive extraction with water and 50 per cent. alcohol. This is contained more largely in the alcoholic extract; the total yield of the pure substance was about 1 gram per kilo. of the leaves. It forms white crystals, which, when anhydrous (from chloroform-alcohol solution), are still unmelted at 240°, but otherwise (from 85 per cent. alcohol) soften at 145—150°. When hydrolysed with alcoholic hydrochloric acid, it yields β-digitogenin, $C_{21}H_{32}O_4$, and a substance, *digitoxose*, which crystallises after the manner of glucose, but was found, unexpectedly, to have the composition $C_6H_{12}O_4$.

Schmiedeberg's "digitoxin" was probably an impure specimen of the substance described above; the author proposes to call it, provisionally, α-digitoxin, distinguishing his own compound by the prefix β. C. F. B.

**Quassole, a Substance accompanying Quassin.** By E. Merck (*Chem. Centr.*, 1895, i, 435; from *Ber. ü. d. Jahr.*, 1894, 19—20).—*Quassole*, $C_{40}H_{70}O + H_2O$ (?), is obtained from crude quassin by extraction with ether; it crystallises in colourless plates, and melts at 149—151°. In a mixture of ether and chloroform $[\alpha]_D = -42·6°$, and in chloroform alone $= -46°$. In alcoholic solution, it gives a pale yellow coloration with ferric chloride; in chloroform solution, a deep red coloration with concentrated sulphuric acid, and differs from quassin by its absence of taste. Quassole dissolves in fuming nitric acid, but the ordinary concentrated acid is apparently without action. J. B. T.

**Artemisin, a Substance accompanying Santonin.** By E. Merck (*Chem. Centr.*, 1895, i, 436; from *Ber. ü. d. Jahr.*, 1894, 3—6).—*Artemisin*, $C_{15}H_{18}O_4$, is obtained from the last mother liquors in the technical treatment of the seed of *Artemisia maritima*. It is freed from santonin by recrystallisation from chloroform, being deposited in combination with 1 mol. of the solvent, which is evolved at 90°. It melts at 200°, gradually turns yellow in the air, and is more readily soluble in water and dilute alcohol than santonin; $[\alpha]_D = -84·3°$. The ferric chloride reaction is not characteristic; when heated with soda (10 parts) and water (40 parts), a fugitive carmine-red coloration is produced, and, like santonin, it gives the same colour with alcoholic soda. Artemisin is apparently a hydroxysantonin.

J. B. T.

**Physcihydrone and Protophyscihydrone.** By OSWALD HESSE (*Annalen*, 1895, **286**, 376; compare Abstr., 1895, i, 300).—Physcihydrone has the composition $C_{16}H_{14}O_4$, and protophyscihydrone the formula $C_{15}H_{12}O_4$.

M. O. F.

**Phenylcoumalin and Pseudodicotoïn.** By OSWALD HESSE (*Ber.*, 1895, **28**, 2507—2509).—In reply to Ciamician and Silber (Abstr., 1895, i, 554), the author states that he was the first to show that "dicotoïn" is a compound of cotoïn and phenylcoumalin. The melting point of phenylcoumalin is still given as 61°, whereas Ciamician and Silber give 68°. The investigation of Tod's pseudo-dicotoïn cannot be continued for lack of material.

J. J. S.

**Derivatives of Cinchomeronic acid.** By SIEGFRIED BLUMENFELD (*Monatsh.*, 1895, **16**, 693—720; compare Meyer, Abstr., 1894, i, 425, and Pollak, Abstr., 1895, i, 391).—*Diethylic cinchomeronate*, $C_5NH_3(COOEt)_2$ is conveniently prepared by the further ethylation of Strache's ethylic hydrogen cinchomeronate (compare Abstr., 1890, 1157). It is a colourless, odourless oil, having a burning taste and turning yellow on exposure to light; it decomposes when distilled under ordinary pressure, boils at 172·1° (corr.) under a pressure of 21 mm., and does not solidify at −60°. It mixes with alcohol, ether, benzene, xylene, and light petroleum in all proportions, gives a *platinochloride*, $2C_5NH_3(COOEt)_2,H_2PtCl_6$, which crystallises in small, yellow needles, and melts and decomposes at 142—144°. It forms alkyl additive products, which, on hydrolysis with silver oxide, yield the ethylbetaïne of cinchomeronic acid, $C_9H_9NO_4$, a compound analogous to apophyllenic acid (compare Roser, *Annalen*, 1886, **234**, 119), and from which the *silver salt*, $C_9H_8AgNO_4$, crystallising in long, slender, colourless needles, and the *hydrochloride*, $C_9H_9NO_4,HCl$, melting with decomposition at 214—216°, may be formed.

*Cinchomeronamide*, $C_5NH_3(CONH_2)_2$, obtained in quantitative yield by the action of ammonia on diethylic cinchomeronate, is insoluble in benzene and ether, dissolves in water and ethylic alcohol, melts with evolution of gas at 163—165°, again solidifies, and finally melts and decomposes at 225°. With potassium hypobromite, cinchomeronamide yields both β- and γ-amidopyridinecarboxylic acids in addition to an intermediate product. The hydrochlorides of these carboxylic acids are resolved by the action of heat into β- and γ-amidopyridine respectively.

G. T. M.

**Collidinepiperidine.** By PETER KNUDSEN and RICHARD WOLFFENSTEIN (*Ber.*, 1895, **28**, 2275—2276).—Bromocollidine readily reacts with piperidine to form *collidinepiperidine*, $C_{13}H_{20}N_2$, hydrogen bromide being also formed. The new base boils at 279—282°, and forms a *hydrochloride*, $C_{13}H_{20}N_2,2HCl$. Coniine reacts in a similar manner, the corresponding derivative being formed. The *platinochloride* of *collidineconiïne*, $C_{16}H_{26}N_2,2H_2PtCl_6$, crystallises in small, red prisms, and melts and decomposes at 244—245°. The authors assume that the bromine removes the hydrogen atom combined with the nitrogen of the reduced pyridine base. A. H.

**Quinoline Derivatives substituted in the Nitrogen Ring.** By ALFRED EINHORN and PENOYER SHERMAN (*Annalen*, 1895, **287**, 26—49; compare Abstr., 1891, 83).—2′-Quinolylacrylic acid is the substance employed in the preparation of those compounds described in the present paper; its *barium* salt crystallises in white needles, with $2H_2O$, the *silver* salt darkens when exposed to light, the *ethylic* salt melts at 73°, and the *amide* at 175—176°.

2′-Quinolylpropionic acid melts at 122—123°, and not at 115° as previously stated (*loc. cit.*); the *calcium* salt is anhydrous, the *platinochloride* melts and decomposes at 197°, and the *amide* melts at 149—150°.

2′-*Quinolylpropylic alcohol*, $C_9NH_6\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$. is obtained by reducing 2′-quinolylacrylic acid with sodium amalgam in alkaline solution, or by means of tin and hydrochloric acid; it crystallises from petroleum in lustrous needles, and melts at 115°. Oxidation with potassium permanganate gives rise to 2′-quinolylpropionic acid.

2′-*Quinolylglyceric acid*, $C_9NH_6\cdot CH(OH)\cdot CH(OH)\cdot COOH$, is obtained by oxidising 2′-quinolylacrylic acid with potassium permanganate; it crystallises from dilute alcohol in white leaflets which contain $3H_2O$, and in this condition melts between 100° and 150°, slowly losing water, and becoming black. The *aurochloride* crystallises in yellow prisms, and melts at 174°, the *barium* salt is anhydrous, the *ethylic* salt melts at 107—108°, and the *methylic* salt at 140—141°.

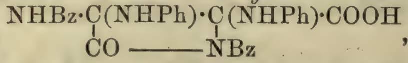
2′-Quinolylacetic acid has been already described (*loc. cit.*); the *platinochloride* is dimorphous, the *methylic* salt melts at 72°, and the *ethylic* salt at 67°.

Much evidence is adduced to show that the product of condensation between 2′-quinolylacetaldehyde and orthamidobenzaldehyde is identical with Weidel's 2′-3′-diquinolyl. M. O. F.

**Hippuroflavin.** By LEOPOLD RÜGHEIMER (*Annalen*, 1895, **287**, 50—97; compare Abstr., 1889, 252, and 1894, i, 55).—The author prefaces the description of his experiments with a discussion of the constitution of hippuroflavin and its derivatives; the structural formula already put forward (*loc. cit.*) continues to be adopted, and attention is drawn to the quinonic character of the substance.

Hippuroflavin (*dibenzoylisopyrazinequinone*), $C_{18}H_{10}N_2O_4$, has been already described in some detail (*loc. cit.*); the following derivatives have been prepared for the first time.

*Dihydrohippuroflavindianilide* (*Dianilidodihydroxydibenzoyl*-nn-*dihydropyrazine*), $C_{30}H_{24}N_4O_4$, is obtained by heating hippuroflavin on the water bath with excess of aniline and glacial acetic acid; it melts and decomposes at 158—160°, and does not dissolve in common solvents, purification being effected by converting it into the *potassium* salt, which is then decomposed by the addition of water to the alcoholic solution.

When caustic soda is added in small quantities to dianilidohippuroflavin suspended in warm water, the *amidanhydride* of dibenzylamidodianilidosuccinic acid,  $\begin{array}{l}\mathrm{NHBz{\cdot}C(NHPh){\cdot}C(NHPh){\cdot}COOH}\\ \qquad\quad\,|\qquad\qquad\quad\;\;|\\ \qquad\;\mathrm{CO}\text{———}\mathrm{NBz}\end{array}$, is formed; the solid product obtained on acidifying the filtered liquid is dissolved in ammonia, and treated with calcium chloride, in order to remove the acid as *calcium* salt. The amidanhydride crystallises from alcohol in small needles, and melts with effervescence at 226—227°; the *calcium* salt forms slender, colourless needles, containing $3H_2O$, and precipitates are formed when a neutral solution of the ammonium salt is treated with solutions of metallic salts.

*Dihydrohippuroflavinbismethylanilide* (*dimethylanilidodihydroxydibenzoyl*-nn-*dihydropyrazine*), $C_{32}H_{28}N_4O_4$ is obtained from hippuroflavin and methylaniline; it melts at 238°, previously becoming dark yellow.

*Hippuroflavinbismethylanilide*, $C_{32}H_{26}N_4O_4$, is obtained from the foregoing substance by the action of boiling nitrobenzene; it melts at 233—234°.

*Dihydrohippuroflavindiorthotoluidide* (*diorthotoluidobenzoyldihydroxy*-nn-*dihydropyrazine*), $C_{32}H_{28}N_4O_4$, is colourless, and melts at 235—238°, yielding orthotoluidine and *hippuroflavinorthotoluidide*, $C_{25}H_{19}N_3O_4$, which crystallises from benzene in stellate aggregates of needles, and melts at 208—209°.

*Hippuroflavinparatoluidide*, $C_{25}H_{19}N_3O_4$ and *hippuroflavinxylidide* melt at 246° and 223—225° respectively.

*Dihydrohippuroflavindiamide* (*diamidodibenzoyldihydroxy*-nn-*dihydropyrazine*), $C_{18}H_{16}N_4O_4$, is obtained by the action of ammonia on hippuroflavin; it melts at 240°, and begins to darken at 220—225°.

*Hippuroflavindiamide*, $C_{18}H_{14}N_4O_4$ is obtained by treating the foregoing compound with alcoholic ammonia in sealed tubes at 105°, for four hours; it melts at 237—238°. M. O. F.

**Two new Bases in the Urine of the Insane.** By MARTIN KRÜGER (*Chem. Centr.*, 1895, i, 292—293; from *Du Bois-Reymond's Arch.*, 1894, 553—555).—The one base, $C_{10}H_{13}N_9O_2$, is, from its resemblance to guanine, termed *epiguanine*, and crystallises from water in slender needles, and from highly dilute ammonia in silky, lustrous prisms; it dissolves in acids, in sodium carbonate solution, and in soda; from the last solvent, lustrous, broad needles are deposited, which probably consist of a sodium derivative. The *nitrate* forms polyhedral crystals; the *chromate* is deposited in lustrous prisms, the *platinochloride* in long, orange-red prisms. The *picrate* and *aurochloride* crystallise in needles. The base gives precipitates with ammonia, silver nitrate, copper sulphate, and sodium hydrogen sulphite, but not with mercuric chloride, normal, basic, or ammoniacal lead acetate. The second base was obtained only in very small quantity from the mother liquor of epiguanine. J. B. T.

**Hydrogenation of Quinine.** By EDUARD LIPPMANN and FRANZ FLEISSNER (*Monatsh.*, 1895, **16**, 630—637).—When dissolved in absolute alcohol and treated with metallic sodium, quinine yields a reduction product which is apparently a tetrahydroquinine. It is an amorphous, brittle mass, which is sparingly dissolved by water, but is exceedingly soluble in alcohol, benzene, and chloroform. The base has the odour of quinoline, yields fluorescent solutions when dissolved in sulphuric acid and nitric acid, and gives the quinine reaction with ammonia and chlorine water. With a feebly acid solution, ferric chloride gives an intense green coloration, which on further addition of the reagent turns reddish-brown. These colour reactions are characteristic of the base, which also forms the following unstable salts: a *normal hydrochloride*, $C_{20}H_{28}N_2O_2,HCl + H_2O$, an *acid hydrochloride*, a *normal sulphate*, an *acid sulphate*, and a *platinochloride*, $C_{20}H_{28}N_2O_2,H_2PtCl_6$. On heating with excess of acetic anhydride, only one acetyl group enters the molecule, the compound $C_{20}H_{27}AcO_2N_2$, being formed as a viscous mass. Tetrahydroquinine therefore contains only one hydroxyl group, and from its behaviour with hydrochloric acid, whereby hydrochlorohydroapoquinine is formed, it would appear that the double linkage existing between the carbon atoms in quinine is not broken away during the addition of the four atoms of hydrogen.

Hydroquinine has a powerful toxic effect, small doses causing suspension of respiration with loss of voluntary and reflex movement, and ultimately convulsions and death. G. T. M.

**Merochinine.** By WILHELM KOENIGS (*Ber.*, 1895, **28**, 1986—1991).—Merochinine, which is obtained, as already described by the author (Abstr., 1894, i, 392, 477), by the hydrolytic decomposition of cinchine and chinine, and by the direct oxidation of cinchonine with chromic acid, is converted into 3 : 2-methylethylpyridine by heating with hydrochloric acid and mercuric chloride at 250°. As it also contains the imido-group, it is in all probability the carboxylic acid of a hydropyridine base of the formula $C_8H_{15}N$. All attempts to convert it into the corresponding pyridinecarboxylic acid by removal of hydrogen or by elimination of hydrogen bromide from bromomerochinine have been unsuccessful, as the carboxyl group is in all cases simultaneously eliminated. When oxidised with potassium permanganate, it is converted into cincholeuponic acid, and the carboxyl group must therefore occupy the same position as one of the carboxyl groups of the latter compound.

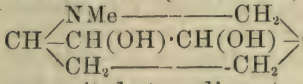
From his researches, Skraup has concluded that in the so-called "second residue" of the cinchona alkaloïds, a vinyl group is combined with one of the carbon atoms of the hydropyridine ring, and this conclusion has been supported by von Miller and Rohde (Abstr., 1895, i, 435); in that case, merochinine, which is obtained from this second residue, would also contain the vinyl group, probably in combination with the 2-carbon atom of the pyridine group. The presence of this group in cinchonine is borne out by the following results. The author and Comstock have shown (Abstr., 1887, 281) that cinchonine readily combines with 2 atoms of bromine, and on treatment with boiling alcoholic potash the product loses 2 mols. of hydrogen bromide, forming dehydrocinchonine, which must therefore either contain two ethylene linkages or an acetylene linkage. No direct proof of the presence of the latter has been obtained, but it is found that, on oxidation, one carbon atom of dehydrocinchonine is eliminated as carbonic anhydride, with formation of cinchotenine. The latter has been also obtained by Skraup by the oxidation of cinchonine; it is a saturated compound, and contains a carboxyl group, in addition to the hydroxyl group of the cinchonine, and therefore the dehydrocinchonine, from which it is prepared, cannot contain two ethylene linkages, but must contain an acetylene linkage, which is formed from the vinyl group of cinchonine by removal of hydrogen.

*Bromomerochinine hydrobromide*, $C_9NH_{14}BrO_2,HBr$, is obtained by the action of bromine water on merochinine, and is identical with the compound obtained by Comstock and Koenigs by the action of bromine water on the bye-products of the oxidation of quinine and cinchonine with chromic acid, and to which they at that time ascribed the formula $C_9NH_{13}Br_2O + \frac{1}{2}H_2O$. It forms rhombic sphenoïds, melts and decomposes at 248—250°, and is reconverted into merochinine by treatment with zinc dust and sulphuric acid, all attempts, however, to convert it into a pyridine or lower hydropyridine derivative were without success.

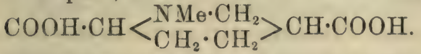
When bromomerochinine hydrobromide is boiled with water, it readily loses one atom of bromine, and on long-continued boiling the second bromine atom is eliminated, *hydroxymerochinine*, $C_9NH_{15}O_3$, being formed. On adding ether to a solution of this compound in methylic alcohol, it crystallises out with $1H_2O$; this is evolved at 110°, the anhydrous substance melting and decomposing at 254°. The *hydrochloride*, $C_9NH_{15}O_3,HCl$, forms stellate groups of needles melting at 208—210°; the *platinochloride* small, lustrous, orange-yellow crystals melting and decomposing at 240°; and the *aurochloride* needles melting and decomposing at 181°. The *acetyl* derivative is very soluble in water and alcohol, and yields an *aurochloride* which melts at 214°, with evolution of gas. It is only oxidised by alkaline potassium permanganate on warming, whilst merochinine and bromomerochinine are oxidised in the cold, and whereas merochinine readily undergoes etherification when hydrogen chloride is passed into its solution in methylic alcohol, the bromo- and hydroxy-derivatives can only be etherified with difficulty in this way.

Higher brominated derivatives of merochinine may be obtained by heating bromomerochinine hydrobromide with bromine at 100°, or by the action of bromine on the hydrochloride of merochinine ethylic ether in chloroform solution. One of these is a colourless, crystalline compound melting and decomposing at 184°, and is the hydrobromide of either a tribromomerochinine, or of a monobromomerochinine dibromide. H. G. C.

**New Methods for the Preparation of Tropinic acid.** By RICHARD WILLSTÄTTER (*Ber.*, 1895, **28**, 2277—2280).—Dihydroxytropidine,



contains two hydroxyl groups, which are united to adjacent carbon atoms; and when treated with chromic acid, it is converted into tropinic acid, identical with that obtained by the oxidation of tropine. This proves that two adjacent carbon atoms of dihydroxytropidine, and therefore also of tropine, serve to form the two carboxyl groups of tropinic acid,



$COOH{\cdot}CH<^{NMe\cdot CH_2}_{CH_2\cdot CH_2}>CH{\cdot}COOH$.

This is in agreement with the above formula proposed for the acid by Merling (Abstr., 1892, 358), whilst it is inconsistent with Ladenburg's formula for the same substance. A. H.

**Scopoleïnes (Ethereal Salts of Scopoline).** By E. MERCK (*Chem. Centr.*, 1895, i, 434—435; from *Ber. ü. d. Jahr.*, 1894, 15—18).—The only scopoleïne found in nature is scopolamine, the scopoleïne of tropic acid, which occurs in *Scopolia japonica* and *S. atropoides*, and is identical with hyoscine. *Acetylscopoleïne*, $C_8H_{12}NO_2Ac$, forms white crystals melting at 250°; the *aurochloride* melts at 195—197°. *Benzoylscopoleïne*, $C_8H_{12}NO_2Bz$, is crystalline, and melts at 68—70°; the *hydrochloride* melts and decomposes at 249—250°; the *hydrobromide* crystallises in colourless prisms melting at 245—247°; the *nitrate*, *platinochloride* (m. p. 200—201°), *aurochloride* (m. p. 188°), *mercurochloride* (m. p. 140—142°), and *picrate* (m. p. 200—201°) have also been prepared. *Cinnamoylscopoleïne*,

$$C_8H_{12}NO_2{\cdot}CO{\cdot}CH{:}CHPh,$$

slowly becomes crystalline; its *nitrate* melts at 172—173°; the *hydrobromide* has also been prepared. J. B. T.

**Tropeïnes.** By E. MERCK (*Chem. Centr.*, 1895, i, 434; from *Ber. ü. d. Jahr.*, 1894, 7—11).—The object of this investigation was the determination of the physiological action of the fatty acid derivatives of tropeïne. The majority have no special influence; lactyltropeïne exercises a well-marked effect on the heart, but it is not a mydriatic. *Acetyltropeïne*, $C_8H_4NOAc$, is a pale yellow syrup, boiling at 235—237°; the *aurochloride* melts at 193°. *Lactyltropeïne*, $C_8H_{14}NO{\cdot}CO{\cdot}CHMe{\cdot}OH$, crystallises in colourless needles, and melts at 74—75°; its *hydrochloride*, *hydriodide*, *nitrate*, *sulphate*, and *aurochloride* (m. p. 143—146°) have been prepared. *Succinyltropeïne*, $C_2H_4(CO{\cdot}C_8H_4NO)_2$, yields a *hydrobromide* and an *aurochloride*; the former is colourless; the latter crystallises in yellow plates. The same derivatives of *malyl-*, *tartryl-*, and *hippuryl-tropeïne* have also been prepared; the *aurochlorides* melt at 203—204°, 233°, and 190—192° respectively. Tartryltropeïne is colourless and crystalline. *Paramethylhomoatropine*, $C_8H_{14}NO{\cdot}CO{\cdot}CH(OH){\cdot}C_6H_4Me$, prepared by the action of dilute hydrochloric acid on tropine paramethylmandelate, is crystalline; its *aurochloride* melts at 192—193°. J. B. T.

**Angostura Alkaloïds.** By HEINRICH BECKURTS (*Arch. Pharm.*, 1895, **233**, 410—423).—The alkaloïds cusparine, cusparadine, galipine, and galipidine are obtained together from the ethereal extract of the bark of *Cusparia trifoliata*, Engler (*Galipea officinalis*, Hancock) (Abstr., 1892, 642). Derivatives of cusparine only are described in the present communication. The purification of this compound from traces of galipine is extremely difficult, and is best accomplished by repeated recrystallisation from light petroleum; criteria of its purity are its melting point (89°) and the formation of colourless salts with acids. The alkaloïd gives the following colour reactions. With concentrated sulphuric acid, a dull red, changing to cherry colour. Fuming nitric acid produces a yellow solution; the residue, after evaporation and treatment with potash, becomes orange. Fröhde's reagent gives a brown solution, which changes successively to violet, bluish-green, and deep blue; when warmed, the blue colour is obtained more readily, and it is produced immediately with the concentrated reagent. Sulphuric acid containing titanic anhydride and furfuraldehyde respectively gives a reddish-brown and a brownish-red solution. By the action of bromine water on cusparine hydrobromide, the *dibromide*, $C_{20}H_{19}NO_3,HBr,Br_2$, is formed as a pale yellow, amorphous powder melting at 117°; when treated with alcohol, hard yellow prismatic needles are obtained; they melt at 236°, and probably consist of *cusparine dibromide*, $C_{20}H_{19}NO_3,Br_2$. The platinochloride crystallises with $6H_2O$. *Cusparine methochloride*, $C_{20}H_{19}NO_3MeCl$, prepared from the methiodide (*loc. cit.*), crystallises in lemon-coloured needles and melts at 190°. Its *platinochloride*, $(C_{20}H_{19}NO_3Me)_2PtCl_6$, is deposited in lustrous golden needles melting at 210°; the *aurochloride* forms reddish-brown needles and melts at 152—153°.

*Methylcusparine*, $C_{20}H_{18}NO_3Me + \frac{1}{2}H_2O$, is prepared by the action of potash or silver oxide on cusparine methiodide; it crystallises from dilute alcohol in colourless needles, from water in pearly lustrous plates, and melts at 190°. The *hydrobromide* crystallises with $10H_2O$ in slender, lustrous, yellowish-green plates. The *hydrochloride* crystallises with $2·5H_2O$ in hard, stellate needles. The *platinochloride*, $(C_{20}H_{18}NO_3Me)_2,H_2PtCl_6$, forms golden, lustrous needles and plates melting at 210°. The *methiodide*, $C_{20}H_{18}NO_3Me,MeI$, crystallises in slender, yellow, lustrous needles; it melts at 185°, darkens on exposure to light, and has an intensely bitter taste.

*Cusparine ethiodide*, $C_{20}H_{19}NO_3,EtI$, is deposited in yellow, lustrous needles, darkens when exposed to light, and melts at 201°. The *chloride* crystallises in lemon-coloured needles melting at 156°. The *platinochloride* is deposited in golden, stellate, rhombic prisms melting at 178°. *Ethylcusparine*, $C_{20}H_{18}NO_3Et$, prepared by the action of soda on the ethiodide, crystallises in colourless, transparent prisms, and melts at 190—191°. The same compound, together with the *hydrate*, $C_{20}H_{18}NO_3Et + H_2O$, is formed by the interaction of the ethiodide and silver oxide; it crystallises in lustrous plates, and melts at 114—115°.

J. B. T.

**Alkaloïds of Berberis Aquifolium.** By H. POMMEREHNE (*Arch. Pharm.*, 1895, **233**, 127—174).—The pulverised root of *Berberis* *aquifolium* was repeatedly extracted with water containing a little acetic acid, the extract was concentrated and filtered from berberine acetate and other substances, and from the filtrate, by saturating it with sodium sulphate, oxyacanthine was eventually obtained, whilst berbamine was obtained by saturating the filtrate from the oxyacanthine with sodium nitrate. These two alkaloïds were then purified by crystallisation of their hydrochlorides from water. New experiments were made with them, and some hitherto doubtful points finally decided. Some properties of berberine, as to which contradictory statements exist, were also re-examined.

*Oxyacanthine.*—This substance has the composition $C_{19}H_{21}NO_3$; it is a monacid base, and is identical in composition and properties with the product obtained by Hesse from *B. vulgaris*. It can be obtained as a white, amorphous precipitate, which melts at 150—160°; or, by crystallisation from 90 per cent. alcohol, in colourless crystals which melt at 208—210°. In alcoholic solution at 20°, it has the specific rotation $[\alpha]_D = +174° 5'$, and it forms a well crystallised compound with lævo-, but not with dextro-, rotatory tartaric acid. It contains an hydroxyl group, for, although acetic chloride and acetic anhydride seem to exercise a dehydrating action on it, yet benzoic chloride converts it into a *monobenzoyl derivative*, of which the *platinochloride*, with $8H_2O$, and *aurochloride*, with $2H_2O$, were prepared. It probably contains 2 methoxyl groups; the numbers obtained by Zeisel's method point, curiously enough, to $1\frac{1}{2}$. It reacts as a tertiary base with *methylic iodide*, yielding an *additive compound*,

$$C_{19}H_{21}NO_3,MeI + 2H_2O;$$

half of the water is lost at 100°, the rest at 110°; it melts when anhydrous at 248—250°, and can be converted by means of silver oxide into an alkaline quaternary ammonium base, the *platinochloride*, with $5H_2O$, and *aurochloride*, with $H_2O$, of which were prepared. Oxyacanthine gives the usual alkaloïd reactions. The following salts were prepared and analysed:—Hydrochloride, specific rotation $[\alpha]_D = +163° 49'$, *hydrobromide*, *hydriodide* melting at 256—258°, *nitrate*, all with $2H_2O$; normal sulphate, aurochloride, both with $4H_2O$; platinochloride with $5H_2O$.

*Berbamine.*—This has the composition $C_{18}H_{19}NO_3$, as was shown by the analysis of its *hydrochloride*, with $2H_2O$, and platinochloride, with $5H_2O$. It was obtained in small quantity only, and appears to contain 1—2 methoxyl groups.

*Berberine.*—This alkaloïd yields a normal sulphate, with $3H_2O$, in addition to the hydrogen sulphate; it also forms a stable hydrogen carbonate, $C_{20}H_{17}NO_4,H_2CO_3 + 2H_2O$, and a stable hydrocyanide. Methylic, ethylic, and amylic iodides form additive compounds with berberine, but these quaternary ammonium derivatives are not very stable; they do not yield the corresponding chlorides when treated with silver chloride, berberine hydrochloride being formed instead.

C. F. B.

**Identity of Baptitoxine and Cytisine.** By Pieter C. Plugge (*Arch. Pharm.*, 1895, **233**, 294—299).—Baptitoxine, obtained by von Schroeder from the root of *Baptisia tinctoria*, is shown to be identical with cytisine. The seeds afford a better source of the alkaloïd; those of *B. australis* contain 2·85 per cent. of cytisine, and those of *B. tinctoria* probably an equal amount. C. F. B.

**Estimation of Alkyl Groups attached to Nitrogen.** By JOSEF HERZIG and HANS MEYER (*Monatsh.*, 1895, **16**, 599—608; compare Abstr., 1894, ii, 219; 1895, i, 310).—The authors have previously (*loc. cit.*) described a method for the detection and estimation of alkyl groups attached to nitrogen, and have shown that, by a modification of the process, the methoxyl and ethoxyl groups present can also be determined. A large number of substances have now been examined, and the results obtained in part agree with accepted constitutions, and in other cases contradict them.

The alkaloïds, harmine and harmaline, each contains one methoxyl group, but no methyl attached to nitrogen (compare Fischer, Abstr., 1889, 730, and Fischer and Täuber, Abstr., 1885, 820).

Sparteïne contains no methyl group attached to nitrogen (compare Ahrens, Abstr., 1888, 611), and Ahrens' norsparteïne is only an impure form of sparteïne.

Pilocarpine contains only one methyl group attached to nitrogen and no methoxyl group, the authors therefore conclude that either Hardy and Calmel's formula, which gives three methyl groups directly attached to nitrogen must be incorrect, or that their method of estimation is unsuited to this compound.

The methyl derivative of the methylbetaïne of papaverinic acid, which melts at 126°, contains four methoxyl groups (compare Schranzhofer, Abstr., 1894, i, 59 and 151). G. T. M.

**Pauçine.** By E. MERCK (*Chem. Centr.*, 1895, i, 434, from *Ber. ü. d. Jahr.*, 1894, 11—15).—*Pauçine*, $C_{27}H_{39}N_5O_5 + 6·5H_2O$, is the alkaloïd of the "pauço nut," the fruit of *Pentaclethra macrophylla;* it crystallises in golden plates, melts at 126°, is insoluble in ether and chloroform, and a portion is decomposed when it is recrystallised from water. The *hydrochloride*, $C_{27}H_{39}N_5O_5,2HCl + 6H_2O$, melts at 245—247°. The *platinochloride*, $C_{27}H_{39}N_5O_5.H_2PtCl_6 + 6H_2O$, is brownish-red, crystalline, and melts at 145°. The *picrate* crystallises in garnet-red prisms melting at 220°. By the action on pauçine, of potash, or of concentrated hydrochloric acid, at 150°, dimethylamine is eliminated. J. B. T.

**Matrine, the Alkaloïd of Sophora Angustifolia.** By PIETER C. PLUGGE (*Arch. Pharm.*, 1895, **233**, 441—443).—Nagai has recently published, in Japanese, a communication on the alkaloïd in the root of *Sophora angustifolia*, which he terms *matrine*, $C_{15}H_{24}N_2O$; it melts at about 80°, is, in aqueous solution, dextrogyrate, and gives precipitates, which are frequently crystalline, with the usual alkaloïd reagents. The *platinochloride*, $C_{15}H_{24}N_2O.H_2PtCl_6$, and the *aurochloride*, $C_{15}H_{24}N_2O,HAuCl_4$, have been prepared by Nagai, and the author has obtained a crystalline *ferrocyanide*. The lethal dose of matrine is larger than that of cytisine, and the compounds differ in physiological action. J. B. T.

# Organic Chemistry.

**Explosive Double Salt of Potassium Cyanide and Potassium Nitrite.** By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1895, **10**, 259—261).—A good yield of sodium nitroferrocyanide is obtained by the action of a concentrated solution of ferrous sulphate on an aqueous solution containing equal weights of sodium nitrite and potassium cyanide. With the object of obtaining an intermediate compound, which, by the action of ferrous sulphate, is converted into the nitroferrocyanide, the author has examined the action of potassium cyanide on potassium nitrite.

When a solution of the two salts is boiled, the cyanide is converted into ammonia, and potassium carbonate, formate, and nitrate.

The *double salt*, $KCN,KNO_2 + \frac{1}{2}H_2O$, is obtained by dissolving potassium nitrite (50 grams) and potassium cyanide (20 grams) in the smallest possible quantity of water and allowing the solution to evaporate over sulphuric acid. Potassium cyanide separates first, and then the new double salt in short, characteristic prisms. It explodes with a loud report when heated at 400—500°, but does not explode on percussion; on recrystallisation in a vacuum over sulphuric acid, it is partially decomposed into its component salts. With silver nitrate, the neutral solution gives silver cyanide and silver nitrite.

E. C. R.

**Sodium Nitroferrocyanide.** By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1895, **10**, 262—276).—*Sodium amidoferrocyanide*,

$$FeC_5N_6H_2Na_3,2\frac{1}{2}H_2O,$$

is obtained by reducing sodium nitroferrocyanide with 4 per cent. sodium amalgam, cooling the mixture with ice and salt; the product is precipitated with alcohol, re-dissolved in ice-cold water, and again precipitated. It crystallises in bright yellow needles, and its solution decomposes at the ordinary temperature yielding ammonia, ferric hydroxide, and sodium ferrocyanide. With bleaching powder and dilute sulphuric acid, it gives a beautiful reddish-violet solution; with ferrous sulphate, a bright greenish-blue precipitate; with ferric chloride, a deep blue-green precipitate; and with dilute hydrochloric acid, a green solution. When heated with sodium hydroxide, it yields ammonia, ferric hydroxide, and sodium ferrocyanide; when heated with hydroxylamine and dilute sodium hydroxide, it gives a reddish-yellow, and then a beautiful, bluish-red solution. The same compound is also obtained when a solution of sodium nitroferrocyanide, cooled with ice and salt, is treated with gaseous ammonia; the product obtained crystallised, however, with $6H_2O$. The *silver salt*, $FeC_5N_6H_2Ag_3,3H_2O$, is obtained in white aggregates by adding silver nitrate to the aqueous solution in the presence of neutral ammonium nitrate; when treated with methylic iodide, decomposition takes place, and a residue, containing iron and cyanogen together with methylcarbylamine, is formed. The formation of amidoferrocyanide from nitroferrocyanide is a reduction process and not a substitution process; for amidoferrocyanide is formed by the action of mono- and diethylamine, as well as by that of ammonia. When preparing the compound by the action of these amines, hydrates, with $5H_2O$ and $7H_2O$, were obtained. When nitroferrocyanide is treated with pure trimethylamine, a brisk evolution of nitrogen takes place, and sodium ferrocyanide and ferric hydroxide are formed; when a 10 per cent. alcoholic solution of trimethylamine is employed, amidoferrocyanide is formed. Sodium amidoferrocyanide is either not altered or entirely decomposed by acetic anhydride, benzenesulphonic chloride, alcohol and carbon bisulphide or chloroform. When treated with iodine dissolved in potassium iodide or in alcohol, it gives a beautiful violet-red compound which easily decomposes into sodium ferrocyanide, ferric hydroxide, nitrogen, and ammonia. If continuously oxidised with potassium permanganate in alkaline solution at the temperature of melting ice, it yields sodium nitroferrocyanide. When treated with nitric oxide in ice-cold aqueous solution, it yields the sodium nitroferrocyanide, $FeC_5N_6Na_4O_2H,7H_2O$, which crystallises in yellow needles, and loses $4\frac{1}{2}$ mols. of water when allowed to remain over sulphuric acid at 50°. When the amidoferrocyanide (6 grams) is treated with sodium nitrite (1·2 grams) in ice-cold aqueous solution, and then acidified with acetic acid, a brisk evolution of gas, containing nitric oxide, takes place, and the solution turns violet-red; when this solution is made slightly alkaline and precipitated with alcohol, the *compound*, $(Na_3FeC_5N_5)_2NONa, + 16H_2O$, is obtained. It crystallises in beautiful orange-yellow needles, gives an intense violet coloration with ammonium sulphide, and does not yield ammonia when heated with sodium hydroxide. When treated with sodium nitrite and acetic acid in ice-cold solution, it is converted into sodium nitroferrocyanide. If only 0·95 gram sodium nitrite is used for 6 grams of sodium amidoferrocyanide, the *compound*, $(Na_3FeC_5N_5)_2NH,16H_2O$, is obtained; this crystallises in sulphur-yellow plates, gives a beautiful bluish-red solution with hydroxylamine and sodium hydroxide, a greenish-blue precipitate with ferrous chloride, an intensely blue precipitate with ferric chloride, and a violet solution with sodium nitrite and acetic acid. When heated with sodium hydroxide, it yields ammonia, and with small quantities of sodium nitrite it yields sodium nitroferrocyanide.

From the above reactions, the author points out that the amido-group in amidoferrocyanides behave in a very different manner from amido-groups in organic compounds, and he concludes that it is combined with iron as expressed in the formula $NH_2\cdot Fe(CN)_5Na_3$.

E. C. R.

**Action of Carbonic Anhydride, Water, and Alkalis, on Solutions of Cyanuric acid and Alkali Cyanurates.** By Paul Lemoult (*Compt. rend.*, 1895, **121**, 404—406).—Thermochemical considerations indicate that carbonic anhydride should displace sodium from trisodium cyanurate and convert the latter into the monosodium salt, and experiment confirms this conclusion, the monosodium salt being precipitated when the gas is passed into a concentrated solution of the trisodium salt. Further, carbonic anhydride precipitates the acid from a concentrated solution of the monosodium salt.

Direct experiment shows that, in aqueous solution, cyanuric acid is slowly converted into ammonia and carbonic anhydride. It is also found that the residue of thermal effect observed when the acid is neutralised with an alkali is much reduced if neutralisation is effected as rapidly as possible, but is greatly increased if the addition of successive equivalents of alkali is extended over several hours. These results confirm the author's view that the apparent residual heat of neutralisation is a consequence of the partial decomposition of the acid (this vol., ii, 11), this decomposition being accelerated by the presence of an alkali. C. H. B.

**Bivalent Carbon: Chemistry of Cyanogen and Isocyanogen.** By John U. Nef (*Annalen*, 1895, **287**, 265—359; compare Abstr., 1895, i, 3 and 9).—The author's previous investigations on the subject of bivalent carbon have dealt with aromatic and aliphatic members of the isocyanide group, which are represented by the general formula R·N⁚C, and with fulminic acid, which is expressed constitutionally by the formula C⁚NOH. Attention is now directed towards cyanogen and isocyanogen, and regarding as possible the existence of three isomeric substances having the empirical formula $C_2N_2$, namely, cyanogen, N⁚C·C⁚N, cyanisocyanogen, N⁚C·N⁚C, and diisocyanogen, C⁚N·N⁚C (Thiele, Abstr., 1894, i, 61), the author claims to have established by his experiments the conclusion that the cyanides are derivatives of isocyanogen, and that hydrogen cyanide itself must henceforth be looked on as hydrogen isocyanide, HN⁚C. The foundation for this view is strengthened by the striking resemblance between the salts of hydroxyisocyanogen (fulminic acid) and derivatives of hydrogen isocyanide, the similarity being in some cases so close as to have given rise occasionally to confusion between the substances themselves.

If potassium cyanide is, in reality, potassium isocyanide, KN⁚C, the chemical activity of an unsaturated compound will be displayed by this substance, it having been shown (Abstr., 1892, 1438) that the more positive the character of an unsaturated molecule, the more readily will additive compounds be obtained from it. It is shown by the author's investigation that potassium cyanide does actually exhibit such behaviour, forming ethylic cyanimidocarbonate when treated in dilute, aqueous solution with ethylic hypochlorite; this reaction is analogous to the conversion of isonitriles into derivatives of mesoxamide by means of carbonyl chloride (Abstr., 1892, 1438).

*Ethylic cyanimidocarbonate*, C⁚N·C(NH)·OEt, is obtained by adding ethylic hypochlorite (9 grams) to a solution of potassium cyanide (18 grams) in five times the quantity of water, the liquid being constantly agitated, and maintained at a temperature of −10°. After adding about half the quantity of ethylic hypochlorite, the colourless solution becomes turbid owing to the separation of an oil, which is extracted with ether and dried with calcium chloride; on removing the solvent, an oil is obtained having a sweet, but penetrating odour, and on distilling this substance the greater part boils at

50—51° under a pressure of 30 mm., the higher fraction passing over at 80° under a pressure of 26 mm., and solidifying in the condenser. The liquid is ethylic cyanimidocarbonate, the solid being ethylic diimidoxalate, which is produced from the former compound by the action of alkali.

Ethylic cyanimidocarbonate is a colourless oil having a sweet, but penetrating odour; it is sparingly soluble in cold water, and has the sp. gr. = 1·00 at 15°. It boils at 42°, 50°, and 60°, under pressures of 20 mm., 30 mm., and 42 mm., respectively, and when distilled under atmospheric pressure, boils, and slightly decomposes at 133°. After a few days it darkens and ultimately becomes almost black, but the greater part can be recovered on distillation. Prolonged digestion on the water bath with alcoholic potash or sodium ethoxide converts the substance into potassium cyanide, alcohol, and potassium cyanate; aqueous alkalis give rise to ethylic diimidoxalate, alkali cyanide and cyanate. Ethylic cyanimidocarbonate is decomposed by hydrochloric acid into ammonium chloride and ethylic cyanocarbonate; when heated with aniline on the water bath, it yields ammonia, hydrogen cyanide, alcohol, and ammonium cyanide, whilst from the portion of the residue insoluble in cold alcohol, ethylic acetate extracts cyananiline.

*Ethylic diimidoxalate*, $OEt{\cdot}C(NH){\cdot}C(NH){\cdot}OEt$, is obtained by the action of dilute alkalis on ethylic cyanimidocarbonate; it forms heavy colourless crystals which gradually become brown; melts at 38° and has a slightly sweet, peculiar taste. The substance was obtained in an impure state by Pinner and Klein (*Ber.*, 1878, **11**, 1437), who passed cyanogen into alcoholic hydrochloric acid; their preparation was brown and melted at 25°. The pure substance boils at 69°, 80°, and 100° under pressures of 18 mm., 32 mm., and 82 mm., respectively; under atmospheric pressure it boils and slightly decomposes at 172°. It dissolves readily in water at 25°, and on cooling the liquid at 5° it solidifies to a magma of white needles consisting of a *hydrate* which contains $11H_2O$; it dissolves with difficulty in cold ether and water at 12°, calcium chloride completely removing water from the ethereal solution. Mercuric chloride produces a white, insoluble precipitate when added to aqueous ethylic diimidoxalate.

Ethylic diimidoxalate is not converted into a derivative of oxalic acid on treatment with aqueous alkalis, but on adding dilute hydrochloric acid to the salt, heat is developed, ammonium chloride and ethylic oxalate being produced; aniline at the temperature of the water bath gives rise to cyananiline.

Ethylic imidocarbonate, $HN{:}C(OEt)_2$, is obtained by adding ethylic diimidoxalate (25 grams) to an alcoholic solution of sodium ethoxide containing 4 grams of sodium, filtering from sodium cyanide which separates at 60°, and extracting with ether the diluted liquid after treatment with caustic potash; it boils at 62° and 77° under pressures of 36 mm., and 80 mm. respectively, and when distilled under atmospheric pressure, boils and slightly decomposes at 138—140°. The sp. gr. = 0·948 at 23°. Ethylic imidocarbonate has been obtained in an impure state by Sandmeyer, from potassium cyanide, caustic soda, alcohol and chlorine; it is also prepared by gently heating ethylic cyanimidocarbonate with alcoholic sodium ethoxide. When ethylic imidocarbonate is heated with alcoholic potash, potassium cyanate is formed; aqueous alkalis are without action on the substance.

*Ethylic imidoxalate*, OEt·C(NH)·COOEt, is obtained by agitating a solution of ethylic diimidoxalate (48 grams) in water (240 grams) with decinormal hydrochloric acid (333 grams), and extracting the clear, neutral solution with ether; it boils at 73° under a pressure of 18 mm., and under atmospheric pressure at 175°, when it decomposes. Mercuric chloride yields a white precipitate with an aqueous solution of the substance. Very dilute hydrochloric acid converts ethylic monimidoxalate into ethylic oxalate; the hydrochloride of ethylic oxalate is formed when hydrogen chloride is passed into the solution in dry ether, and it is also obtained on submitting ethylic cyanocarbonate to the same treatment. Sodium cyanide and ethylic carbonate are produced when ethylic monimidoxalate is treated with alcoholic sodium ethoxide at −10°.

Alcoholic sodium ethoxide at −10° decomposes benzoic cyanide into ethylic benzoate and sodium cyanide, the same agent converting ethylic cyanocarbonate into hydrogen cyanide and ethylic carbonate; alcoholic hydrogen chloride, however, converts these substances into ethylic benzoylformate and ethylic imidoxalate respectively.

Ethylic cyanimidocarbonate is formed when cyanogen chloride or bromide acts on a dilute, alcoholic solution of potassium cyanide. When chlorine is led into a solution of potassium cyanide in dilute alcohol, cyanogen chloride, ethylic diimidoxalate, and ethylic cyanimidocarbonate are formed, the last named being converted by the alkali into ethylic imidocarbonate. On adding ethylic hypochlorite to dilute alcoholic potassium cyanide at −7°, ethylic diimidoxalate is formed.

*Benzeneazo-imidoformyl cyanide*, NPh:N·C(NH)·C:N, is the yellow substance obtained by Gabriel (Abstr., 1880, 41) on adding a solution of diazobenzene chloride to potassium cyanide dissolved in water, and which he regarded as having the formula NPh:N·C:N + HCN on account of the readiness with which hydrogen cyanide is eliminated; the product of this decomposition is diazobenzene cyanide, NPh:N·C:N (compare Abstr., 1895, i, 348).

*Ethylic ethylimidochlorocarbonate*, NEt:CCl·OEt, is obtained by adding dry ethylic hypochlorite at −5° to ethylic isocyanide at −10 to −15°, in molecular proportion, and maintaining the temperature of the mixture below 0°, it boils at 63° and 68° under pressures of 88 mm. and 100 mm. respectively, and at 126° under atmospheric pressure. The vapour has a penetrating odour resembling that of alkylic isocyanates, and vigorously attacks the eyes. Water and dilute hydrochloric acid slowly decompose ethylic ethylimidochlorocarbonate, giving rise to carbonic anhydride, ethylic chloride, diethylcarbamide, and much ethylurethane. Alcoholic sodium ethoxide converts it into *ethylic ethylimidocarbonate*, which boils at 147°, and *ethylic ethylimidocyanocarbonate* is obtained when ethylic ethylimidochlorocarbonate is added to a solution of potassium cyanide in dilute alcohol; it is an oil which boils at 78° under a pressure of 82 mm., and has a sweet, penetrating odour.

*Ethylimidochloro-formyl cyanide*, $NEt{:}CCl{\cdot}C{:}N$, is obtained by allowing a mixture of cyanogen chloride and ethylic isocyanide, in molecular proportion, to remain in contact for two days, and then raising the temperature for a few minutes to 70°; the portion distilling between 120° and 130° is agitated with very dilute hydrochloric acid, washed, dried, and redistilled. It is a colourless oil which boils at 126°, and has a penetrating odour.

*Trimolecular benzoic cyanide*, $[COPh{\cdot}CN]_3$, is obtained by heating benzoic bromide (21 grams), absolute ether (150 c.c.), and silver cyanide (20 grams) for 10 hours in a reflux apparatus from which moisture is excluded, and which is heated on a water bath at 60°. After removing the ethereal liquid, aqueous potassium cyanide is added to the residue in order to remove silver bromide, and the product is then dissolved in chloroform; it crystallises from hot benzene in pale yellow needles, and melts at 195°. The substance is insoluble in water and ether, but dissolves readily in chloroform and hot benzene; when heated at 300°, it decomposes, yielding benzonitrile. It may also be obtained from ordinary benzoic cyanide by passing hydrogen bromide into the solution in absolute ether.

Dimolecular benzoic cyanide was obtained by Wache on heating an ethereal solution of benzoic cyanide with sodium; it is also formed when benzoic chloride is agitated at −5° with a solution of potassium cyanide in dilute alcohol. It crystallises from alcohol in colourless needles, and melts at 99—100° (Wache observed 95°); under a pressure of 15 mm. it boils at 220°. Ordinary benzoic cyanide is formed when benzoic anhydride and potassium cyanide in molecular proportion are heated at 190°.

When ethylic chlorocarbonate (28·5 grams) is heated with silver cyanide (36·4 grams) for six hours at 130—140°, a mixture of ethylic cyanocarbonate and ethylic isocyanocarbonate is formed.

Ethylic chlorocarbonate (50 grams), when agitated with a solution of potassium cyanide (32 grams) in water (96 grams) and alcohol (25 grams), cooled at −13°, yields ethylic cyanocarbonate and a small quantity of ethylic carbonate; if action proceeds at ordinary temperatures, less ethylic cyanocarbonate is formed, a substance being produced which, in the presence of water or alkalis, yields hydrogen cyanide, potassium chloride, carbonic anhydride, and alcohol.

On agitating a solution of potassium cyanide in 6 parts of water cooled at −10° or −15° whilst carbonyl chloride is slowly added, an additive compound is formed which breaks up spontaneously into hydrogen cyanide, potassium chloride, and potassium carbonate.

In 1857 Cloëz obtained from cyanogen chloride and alcoholic sodium ethoxide, an oil which he regarded as ethylic cyanate (*Compt. rend.*, **44**, 482), and this result was confirmed by Hofmann and Olshausen (*Ber.*, 1870, **3**, 269); subsequently Mulder observed that the action of cyanogen bromide on sodium ethoxide in presence of water gave rise to urethane and the substance isolated by Cloëz, which, however, has the composition $OEt{\cdot}CN,HOEt$, and also a considerable quantity of ethylic cyanurate. Finally, Ponomareff (Abstr., 1882, 937) recorded the formation of an oil which distilled between 90° and 200°, and had a basic odour which disappeared on heating the product in an open basin on the water bath. The author finds, in the first place, that pure cyanogen bromide is without action at 50° on sodium ethoxide suspended in absolute ether and free from alcohol; cyanogen chloride is equally inert, but if alcoholic sodium ethoxide is added to cyanogen bromide or chloride at −8° to −10°, a rise of temperature takes place, and the sole product is ethylic imidocarbonate; if the action proceeds at ordinary temperatures, the yield of ethylic imidocarbonate is diminished, urethane and ethylic cyanurate being formed in small quantity. Ethylic imidocarbonate is produced with a small quantity of urethane when excess of caustic soda or potash is added to a mixture of cyanogen chloride (or bromide), water (5 parts), and alcohol (2 parts) cooled to −5° or −10°, the temperature of the liquid being maintained below 0°; these substances probably arise from the decomposition by water or alcohol of the intermediate product $NH\colon CCl\cdot OEt$. When hydrogen bromide is passed into a solution of cyanogen bromide in absolute ether, a yellowish-white precipitate of imidocarbonyl bromide, $NH\colon CBr_2$, or the hydrobromide, is formed; it is hygroscopic, and fumes in air, yielding carbonic anhydride and ammonium bromide, whilst, in a dry atmosphere, hydrogen bromide is eliminated and cyanogen bromide formed.

*Phenylic imidocarbonate*, $NH\colon C(OPh)_2$, is obtained by adding a solution of phenol (80 grams) and caustic potash (48·6 grams) in 300 c.c. of water to a solution of cyanogen bromide (46 grams) in 2500 c.c. of water at 20°, and crystallises from petroleum in colourless needles melting at 54°; it is insoluble in water, but dissolves readily in organic solvents, excepting petroleum. Dilute hydrochloric acid converts it into phenylic carbonate and ammonium chloride, the action of alcoholic potash gives rise to potassium cyanate, and when heated alone in a dry tube, phenylic imidocarbonate yields phenol and phenylic cyanurate. The observation of Hofmann and Olshausen (*loc. cit.*), who passed cyanogen chloride into alcoholic sodium phenoxide and obtained phenylic cyanurate, is incorrect, neither this substance nor phenylic cyanate being formed; when an alcoholic solution of cyanogen chloride or bromide is treated with aqueous or alcoholic sodium phenoxide, phenylic imidocarbonate is the chief product, *ethylic phenylic imidocarbonate* being also formed; the latter boils at 120° under a pressure of 18 mm. The observation of Hofmann and Olshausen originates in the fact that both this salt and also phenylic imidocarbonate decompose into phenol and phenylic cyanurate when heated at 180°.

When cyanogen is passed into an ice-cold solution of potassium cyanide in dilute alcohol, ethylic cyanimidocarbonate is formed together with a small quantity of ethylic diimidoxalate; when passed into a solution of sodium ethoxide in alcohol at 0°, ethylic diimidoxalate is the sole product.

The author has devised a method of obtaining hydrogen cyanide in the pure state. The slightly abnormal vapour density of former preparations is probably due to the presence of about 2 per cent. of ammonium cyanide, and to remove this impurity, dry hydrogen cyanide obtained from potassium ferrocyanide and sulphuric acid is distilled from phosphoric anhydride, and the vapour, after passing through a tube maintained at 40—50° containing a mixture of glass beads and phosphoric anhydride, enters a long condenser, the distillate being collected in a receiver and protected from moisture by a long tube containing calcium chloride and phosphoric anhydride. The product boils at 25° (corr.), and melts at −12° to −10°, undergoing no change when preserved for many months in closed vessels; the purest specimen previously obtained boiled at 26° (corr.), and melted at −14° (Gautier). In comparison with its salts and the alkylic isocyanides, hydrogen cyanide is a very inert substance; it does not combine with chlorine or hydrogen chloride at low temperatures, and no action takes place when it remains in contact with ethylic hypochlorite for a protracted period at −10°.

The want of harmony among the statements of previous investigators (Pinner, Abstr., 1883, 731 and 1089; and 1895, i, 264; Lengfeld and Stieglitz, Abstr., 1895, i, 277; and Claisen and Matthews, *Ber.*, 1883, **16**, 311), has led the author to study the action of hydrogen chloride on hydrogen cyanide in presence of alcohol, with the result that the following observations have been made. Imidoformyl chloride, $NH\colon CHCl$, is first formed, and unites with hydrogen cyanide forming the compound $NH\colon CH\cdot C(NH)Cl$, which takes up one or two molecular proportions of hydrogen chloride; in presence of alcohol, the product gives rise to the compound $OEt\cdot CH(NH_2)\cdot CCl(NH_2)\cdot OEt$, which is present in the mixture of salts which Pinner obtained. The intermediate compound, $NH\colon CH\cdot C(NH)Cl$, also yields ethylic diethoxyimidoglyoxylate, $CH(OEt)_2\cdot CCl(NH_2)\cdot OEt$, and ethylic diethoxyorthamidoglyoxylate hydrochloride,

$$CH(OEt)_2\cdot C(OEt)_2\cdot NH_2,HCl.$$

This brief summary is much expanded in the original paper, which contains a theoretical discussion of the results obtained.

*Imidoformyl cyanide*, $NH\colon CH\cdot C\colon N$, is prepared in the following manner. Pinner's salt, ethylformimide hydrochloride (*loc. cit.*), obtained by passing hydrogen chloride into a mixture of alcohol with a solution of hydrogen cyanide in absolute ether, is suspended in ether and treated with caustic soda; after removal of solid matter, and evaporation of the ether, an oil is deposited which is a mixture of imidoformyl cyanide, the dialcoholate, and ethylic diethoxyorthamidoglyoxylate. On distillation under reduced pressure the cyanide solidifies in the condenser. Imidoformyl cyanide melts at 87°, and boils at 120—125° without decomposing; it is extremely volatile, and sublimes in closed vessels. The substance is decomposed by caustic soda or dilute hydrochloric acid, yielding ammonia and formic acid, whilst an aqueous solution quickly decomposes when heated in a sealed tube at 100°, yielding formamidine formate and ammonium formate; agitation with caustic soda and benzoic chloride gave rise to benzamide and dibenzoylformamidine. The *silver* derivative of the hydrate of imidoformyl cyanide, $AgC_2N_2H,H_2O$, is formed on adding silver nitrate to the concentrated aqueous solution; it is crystalline and colourless, becoming black when treated with boiling water.

On heating hydrogen cyanide (10 grams) with acetic anhydride (37·4 grams) in a sealed tube for five hours at 190—200°, diacetyldicyanide is formed. When hydrogen cyanide (15 grams) remains in contact with acetic bromide (45·5 grams) for four weeks at the ordinary temperature, a hygroscopic substance is formed which decomposes on treatment with water into hydrogen cyanide, acetic acid, and hydrogen bromide; it probably consists of pyruvimide bromide, NH:CBr·COMe.

The paper concludes with a theoretical discussion of the results described. M. O. F.

**Compounds of Acetone with Polyhydric Alcohols.** By ARTHUR SPEIER (*Ber.*, 1895, **28**, 2531—2534).—*Diacetone-erythritol*, $C_4H_6O_4(C_3H_6)_2$, prepared by Fischer's method (Abstr., 1895, i, 441) from acetone and erythritol, has a bitter taste, melts at 56°, and boils at 105—106° (pressure = 29 mm.). *Diacetonearabitol*, $C_5H_8O_5(C_3H_6)_2$, is a colourless syrup with a bitter taste, and may be distilled under diminished pressure. *Diacetone-adonitol* is also a syrup which has a bitter taste, and boils at 150—155° (pressure = 17 mm.). *Diacetone-dulcitol*, $C_6H_{10}O_6(C_3H_6)_2$, crystallises in prisms, melts at 98°, and boils at 193—195° (pressure = 18 mm.). *Triacetone-sorbitol*, $C_6H_8O_6(C_3H_6)_3$, is a colourless, crystalline mass, which melts at about 40°, and boils at 170—175° (pressure = 25 mm.). *Triacetone-α-glucoheptitol*, $C_7H_{10}O_7(C_3H_6)_3$, is a thick, faintly yellow syrup, which has a bitter taste, and boils at 200—201° (pressure = 24 mm.).

Acetone is thus seen to react much more uniformly with the higher alcohols than does benzaldehyde. A. H.

**Constitution of Pectins.** By CHARLES F. CROSS (*Ber.*, 1895, **28**, 2609—2611).—According to Tromp de Haas and Tollens (this vol., i, 7), the atomic ratio of oxygen to hydrogen in the pectins is very nearly 1 to 2, and the percentage composition of nearly all the substances analysed is very similar to that of the oxycellulose-cellulose series. One specimen of pectin had the composition of the typical lignocellulose, jute fibre, and appears by its reactions to be a soluble lignocellulose free from the substances which usually accompany lignocellulose and react with phloroglucinol and aniline salts. The pectins appear to be distinguished from one another by differences which are quite analogous to those by means of which the various members of the group of celluloses can be distinguished.

A. H.

**Preparation of Ethylamine from Aldehyde-Ammonia.** By FERDINAND JEAN (*Bull. Soc. Chim.*, 1895, [3], **13**, 474; compare Cambier and Brochet, Abstr., 1895, i, 641, and this vol., i, 7).—Ethylamine is readily obtained by reducing aldehyde-ammonia with zinc and hydrochloric acid by Trillat and Fayollat's method. The freshly prepared crystals (10 grams) are mixed with a little water and zinc dust (20 grams), and dilute hydrochloric acid (150 grams, 1 : 3) gradually added during 10 minutes; after the lapse of a further interval of 10 minutes, some concentrated acid (20 grams) is added, and the mixture kept cool at first, but after 45 minutes heated on a water bath; the ethylamine is then liberated by adding sufficient caustic soda to redissolve the zinc hydroxide at first precipitated, and is separated by distillation with steam.

The yield of the hydrochloride is about 30 per cent. of the aldehyde employed. As no appreciable amount of the amine is formed by the action of hydrochloric acid alone, the process seems to be purely one of reduction. JN. W.

**Hexamethylenetetramine Mercurochlorides and Mercuriodide.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1895, [3], **13**, 494—497; compare Abstr., 1895, i, 444).—There are three mercurochlorides of hexamethylenetetramine. The first, $C_6H_{12}N_4,2HgCl_2,H_2O$, obtained by exactly precipitating the aqueous amine with aqueous mercuric chloride in the cold, forms silky, white needles, and is stable at 100°, but at a higher temperature commences to decompose, finally melting at about 208°. It forms a yellowish, amorphous *additive* compound with 1 mol. of bromine at the ordinary temperature.

The second *mercurochloride*, $C_6H_{12}N_4,HCl,2HgCl_2,H_2O$, resembles the first in appearance, and is formed in a similar manner from the hydrochloric acid solution of the amine; it melts sharply at 165°, but becomes solid again at a higher temperature, finally softening at about 210° to a yellowish-grey paste. It also forms an *additive* compound with bromine.

The third *mercurochloride*,

$$(C_6H_{12}N_4,2HgCl_2,H_2O)_2,NH_4Cl,HgCl_2,H_2O,$$

is prepared by adding a concentrated solution of mercuric chloride in ammonium chloride to a boiling solution of hexamethylenetetramine containing ammonium chloride: a precipitate forms at first, but redissolves, and on cooling, the mercurochloride separates in hard, dense, colourless prisms. It is stable at 100°, but commences to decompose at about 168°.

All three mercurochlorides are hydrolysed by water at 100° into formaldehyde, mercuric oxide, and ammonium chloride, and the yellowish powder resulting from their decomposition at a higher temperature consists chiefly of mercuric oxide.

The *mercuriodide*, $C_6H_{12}N_4,2HgI_2,H_2O$, is obtained by adding excess of a solution of potassium mercuriodide in dilute acetic acid to the aqueous amine; the solution is boiled until the precipitate redissolves, and the double salt separates in golden-yellow scales. It softens at 156°, and melts at 165°. JN. W.

**Compounds of Amidoguanidine with the Sugars.** By HEINRICH WOLFF (*Ber.*, 1895, **28**, 2613—2615; compare Abstr., 1894, i, 315).—*Galactoseamidoguanidine chloride* forms rhombic crystals, and is slightly dextrorotatory; *galactoseamidoguanidine sulphate* also forms rhombic crystals, which are sparingly soluble in alcohol. *Lactoseamidoguanidine sulphate* crystallises like the sulphate just described, and is dextrorotatory; the *nitrate* forms microscopic needles, which melt and decompose at about 200°. The free bases obtained from the sulphates by means of baryta are amorphous.

A. H.

**Thiamines.** By FELIX LENGFELD and JULIUS STIEGLITZ (*Ber.*, 1895, **28**, 2742—2744; compare Abstr., 1895, i, 264).—*Thiethylimine*, $(S\colon NEt)_4$, is prepared by the action of ethylamine (10 grams) dissolved in light petroleum (150 grams) on recently prepared sulphur dichloride (7·5 grams) dissolved in light petroleum (20—30 grams). The solutions must be dry, as, in presence of moisture, dark-coloured compounds are formed; the ethylamine hydrochloride is removed by filtration, and the light petroleum distilled under reduced pressure in a stream of nitrogen free from moisture, carbonic anhydride and oxygen. The thioimine is a pale-yellow, mobile oil, with an odour recalling both those of carbylamine and mercaptans; it decomposes when heated, and on standing gradually darkens. Cryoscopic molecular weight determinations agree with the above formula. The light petroleum employed was treated successively with sulphur dichloride, water, potash, dried with potassium hydroxide, and distilled, that portion boiling at 30—40° being employed for the experiments; unless these precautions are adopted the petroleum yields a chloroderivative in small quantity, which cannot be removed from the thioimine.

J. B. T.

**Action of Hydroxylamine Hydrochloride on Isonitrosoacetone.** By MILORAD JOVITSCHITSCH (*Ber.*, 1895, **28**, 2673—2674).—A yellow, amorphous mass is obtained when isonitrosoacetone (acetoneoxime) is warmed with an aqueous solution of hydroxylamine hydrochloride; when recrystallised from water, it forms small, colourless needles, and melts and decomposes at 245—246°. It has the composition $C_6H_9N_3O_3$, is readily dissolved in alkalis yielding a yellow solution, and gives precipitates with solutions of most of the heavy metals. When hydrolysed with 30 per cent. sulphuric acid at 140°, it gives acetic acid, formic acid, a hydroxylamine salt, and ammonia. The substance, $C_6H_9N_3O_3$, is identical with that obtained by Scholl (Abstr., 1891, 287), and the author has discontinued his investigation.

J. J. S.

$\alpha\alpha\beta$-**Trihalogen Butyric acids from the Geometrically Isomeric** $\alpha$-**Halogen Crotonic acids.** By VICTOR VALENTIN (*Ber.*, 1895, **28**, 2661—2665).—Both $\alpha$-chlorocrotonic acids, when suspended in carbon bisulphide, readily absorb chlorine, and form the $\alpha\alpha\beta$-trichlorobutyric acid previously described by Krämer and Pinner (*Ber.*, **3**, 389), Judson (*ibid.*, 785), and Garzarolli-Thurnlakh (this Journal, 1876, ii, 623). When warmed, the sodium salt of this acid rapidly decomposes, evolving carbonic anhydride, and giving Judson's $\alpha\alpha$-dichloropropylene. $\alpha\alpha\beta$-Tribromobutyric acid may be obtained in a similar manner by the addition of 2 atoms of bromine to either of the $\alpha$-bromocrotonic acids (Michael and Pendleton, Abstr., 1888, 1176); an aqueous solution of the sodium salt of the tribromo-acid readily evolves carbonic anhydride, and yields $\alpha\alpha$-dibromopropylene. When the latter is heated for 12 hours at 150° with excess of alcoholic potash, it is almost entirely converted into allylene.

J. J. S.

**α-Dimethylamidocaproic acid.** By EDOUARD DUVILLIER (*Bull. Soc. Chim.*, 1895, [3], **13**, 484—487).—α-Dimethylamidocaproic acid is formed by heating α-bromocaproic acid with aqueous dimethylamine (2 mols.) in a sealed vessel at 100°, the liberated hydrobromic acid combining with the second molecule of the amine; the product is boiled with baryta water to expel the excess of the amine, and the acid obtained by decomposing its silver salt, or better, its copper salt with hydrogen sulphide.

*α-Dimethylamidocaproic acid*, $CH_2Pr{\cdot}CH(NMe_2){\cdot}COOH + 2H_2O$, crystallises in bundles of needles, and is freely soluble in water and alcohol, but insoluble in ether; when heated, it melts and sublimes, but at the same time decomposes; the melting point is not given. The *copper* salt, with $2H_2O$, crystallises in dark blue plates or scales, and melts at 110°, but neither the zinc nor the cadmium salt seems to be capable of existence. The *platinochloride* forms small, clinorhombic, orange prisms, and melts at 108°, at the same time decomposing slightly; the *aurochloride* resembles lead iodide in appearance, and a crystalline *hydrochloride* also appears to exist. JN. W.

**Behaviour of the Alkali Salts of the Fatty Acids and of Soaps in presence of Water.** By FRIEDRICH KRAFFT and H. WIGLOW (*Ber.*, 1895, **28**, 2566—2573, 2573—2582).—III. *The Soaps as Crystalloïds.*—When hot 1 per cent. aqueous solutions of sodium stearate, palmitate, myristate, laurate, elaïdate, and oleate are allowed to cool, crystals begin to form respectively at 60°, 45°, 31·5°, 11°, 35°, and 0°, that is, at temperatures 9·2°, 17°, 23°, 32·6°, 16°, and 14° below the melting points of the corresponding acids. The crystals consist of a mixture of the normal and acid salts; when deposited from more dilute solutions, the crystals contain a smaller proportion of sodium, whilst from a 5 per cent. solution of sodium oleate, the neutral salt separates unchanged.

If the hot aqueous solutions are saturated with carbonic anhydride and allowed to cool, the acid salts separate out; for example, sodium hydrogen palmitate, $C_{16}H_{31}O_2Na,C_{16}H_{32}O_2$. The temperature at which any one of these separates lies above the melting point of the corresponding acid, but below that of the sodium hydrogen salt.

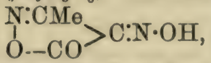
IV. *The Soaps as Colloïds.*—The soaps have been examined with respect to the extent to which they raise the boiling point of water in Beckmann's apparatus. Sodium acetate and propionate act as if each molecule were dissociated into two; but, curiously enough the molecular weight, as calculated from the observed rise of the boiling point, does not increase with increasing concentration, but actually diminishes With sodium caproate, a slight increase is observed; but in very strong solutions the thermometer actually begins to sink again, and the solution solidifies, on cooling, to a gelatinous mass. Sodium nonylate and laurate are comparatively little dissociated in moderately dilute solutions, and their molecular weights increase with increasing concentration to about double the theoretical. Sodium palmitate, stearate, and oleate at first produce a rise in the boiling point, but eventually, as the solutions become more concentrated, the thermometer falls to the boiling point of the water used, and the solutions solidify on cooling to gelatinous masses. The soaps, then, under these circumstances, do not raise the boiling point of water in which they are dissolved, and, so far, exhibit the behaviour of colloïd substances such as gelatin and starch.

C. F. B.

**Derivatives of β-Chlorocrotonic acid.** By Wl. Szenic and R. Taggesell (*Ber.*, 1895, **28**, 2665—2672).—Both Geuther's β-chlorocrotonic acids (*Zeit. für Chemie*, 1871, 240), when dissolved in carbon bisulphide, readily absorb chlorine, and yield *αββ-trichlorobutyric acid*, which crystallises in rhombic plates, and melts at 51·5—52°. It is only sparingly soluble in water, but readily in alcohol, ether, benzene, &c. If an aqueous solution of the trichlorinated acid is treated with granulated zinc and left for several weeks, a mixture of the zinc salts of β-chloroisocrotonic acid and β-chlorocrotonic acid is formed. A solution of sodium trichlorobutyrate, when heated at 100°, evolves carbonic anhydride and yields αβ-dichloropropylene; the latter readily absorbs chlorine, and yields a tetrachloropropane which is identical with that obtained by Borsche and Fittig (*Annalen*, **133**, 114) by the action of phosphorus pentachloride on unsymmetrical dichloracetone. By treating the αββ-trichlorobutyric acid with alcoholic potash, a mixture of two isomeric dichlorocrotonic acids is obtained; the one which is formed in larger quantity melts at 75·5°, and is the centric symmetrical *αβ-dichlorocrotonic acid*. The one formed in smaller quantity melts at 92°, and is identical with the αβ-dichlorocrotonic acid obtained by the addition of two atoms of chlorine to tetrolic acid; it must, therefore, be the plane symmetrical isomeride. The acid melting at 92° is readily converted into tetrolic acid when treated with zinc, whereas the acid melting at 75° is not.

J. J. S.

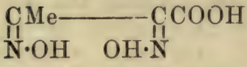
**Action of Hydroxylamine Hydrochloride on Ethylic Isonitrosoacetoacetate.** By Milorad Jovitschitsch (*Ber.*, 1895, **28**, 2675—2683).—By warming ethylic isonitrosoacetoacetate with hydroxylamine hydrochloride, the author has obtained a substance which crystallises in colourless, glistening plates, turns red at 120°, and is completely decomposed at 141—142°; it is readily soluble in ether and in alcohol, sparingly in water, and quite insoluble in light petroleum. It dissolves in alkalis, yielding a deep red solution, but is decomposed when boiled with excess of potassium hydroxide, yielding hydrogen cyanide and the substance $C_6H_9N_3O_3$, this vol., i, 79. Aqueous sulphuric acid also decomposes the compound, yielding hydroxylamine and the compound $C_6H_9N_3O_3$. The author terms the substance *oximidomethylisoxazolone*,



$\begin{array}{l}N{:}CMe\\ |\\ O{-}{-}CO\end{array}\!>C{:}N{\cdot}OH$, and

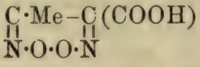
thinks it is identical with the substance previously described by Ceresole and Koeckert (Abstr., 1884, 1120) and by Nussberger (Abstr., 1892, 1175). The silver derivative is obtained as a red, crystalline precipitate on the addition of silver nitrate to the solution of the oxazolone or of its salts. The red precipitate usually contains more or less of a colourless silver salt mixed with it; this colourless salt is more readily soluble in nitric acid than the red one, and the two may be separated by this means. The red salt is explosive, especially when previously heated for some time at 100°. The colourless salt is *silver normal diisonitrosobutyrate;* it readily explodes, and also turns black when heated with water. When warmed with an alkali carbonate, the oximidomethylisoxazolone is rapidly converted into diisonitrosobutyric acid, the silver salt of which, when oxidised with nitric acid (sp. gr. 1·3), yields the peroxide of diisonitrosobutyric acid previously described by Angeli (Abstr., 1893, i, 310). The *silver salt* crystallises in colourless plates, and is explosive; the *ethylic salt* may be obtained by oxidising ethylic diisonitrosobutyrate with nitric acid; it is a thick, oily substance which boils at 240—242°. When silver oximidomethylisoxazolone is oxidised with nitric acid, a small quantity of Angeli's acid is obtained, together with the silver salt of an isomeric acid. This *silver salt* crystallises from water in silky needles. The corresponding acid, $C_4H_4N_2O_4$, differs from Angeli's acid in being only sparingly soluble in ether, in containing no water of crystallisation, and in the sweet taste of its sodium salt.

The following formulæ are given for the various acids:—



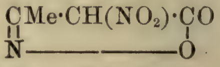
$$\begin{array}{ll} \mathrm{CMe}\text{———}&\mathrm{CCOOH}\\ \| & \| \\ \mathrm{N\cdot OH} & \mathrm{OH\cdot N}\end{array}$$

Syn-diisonitrosobutyric acid.



$$\begin{array}{l} \mathrm{C\cdot Me{-}C(COOH)}\\ \|\qquad\ \ \| \\ \mathrm{N\cdot O\cdot O\cdot N}\end{array}$$

Angeli's peroxide acid.

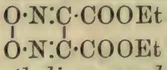


$$\begin{array}{lr} \mathrm{CMe\cdot CH(NO_2)\cdot} & \mathrm{CO}\\ \| & | \\ \mathrm{N}\text{————————} & \mathrm{O}\end{array}$$

Nitromethylisoxazolone.

J. J. S.

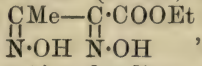
**Preparation of Ethylic Isonitrosoacetoacetate and of an Isomeride from Ethylic Acetoacetate.** By Milorad Jovitschitsch (*Ber.*, 1895, **28**, 2683—2687; compare Abstr., 1878, 396; 1882, 949 and 1052).—The author recommends the following method for the preparation of ethylic isonitrosoacetoacetate. Sodium nitrite (1 mol.) is intimately mixed with ethylic acetoacetate (1 mol.), and to the well-cooled mixture 18 per cent. sulphuric acid ($\frac{1}{2}$ mol.) is slowly run in; after dilution with water, the solution is extracted with ether, the ether evaporated, and the residue dissolved in light petroleum, this solution is then dried with anhydrous sodium sulphate, and, on evaporation, gives a 90 per cent. yield of the isonitroso-compound. When oxidised with nitric acid containing nitrous acid, it yields ethylic oximidonitroacetate (Abstr., 1895, i, 447), which can also be obtained in small quantities directly from ethylic acetoacetate by the action of nitric acid (sp. gr. 1·4) and a small quantity of sodium nitrite in the cold. The chief product of this action, however, is the compound

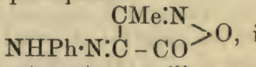
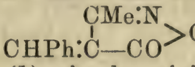


$$\begin{array}{l} \mathrm{O\cdot N{:}C\cdot COOEt}\\ |\qquad\ | \\ \mathrm{O\cdot N{:}C\cdot COOEt}\end{array}$$

(Cramer, Abstr., 1892, 699), which the author terms *ethylic peroxydiisonitrososuccinate.* If, in the above reaction, an excess of sodium nitrite is used, the product formed is a yellow oil, which does not crystallise and has the same percentage composition as ethylic isonitrosoacetoacetate. It differs from its isomeride in the ease with which it is decomposed by dilute alkali, yielding a yellow solution. With hydroxylamine hydrochloride, it yields oximidomethylisoxazolone; on oxidation, it gives the same products as ethylic isonitrosoacetate, and, with phenylhydrazine hydrochloride, it yields 4-oximido-3 : 1-methylphenylpyrazolone. The new isomeride can also be prepared by the action of nitrous acid on ordinary ethylic isonitrosoacetoacetate.

The author considers the two compounds as syn- and anti-isomerides according to Hantzsch's terminology. The new compound is ethylic *syn*-isonitrosoacetoacetate, and the old compound is the *anti*-isomeride. When treated with bromine (1 mol.), the two compounds yield the corresponding monobromo-derivatives; these are both oils, but differ in their action with alkalis. J. J. S.

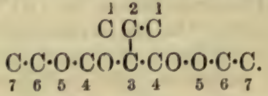
**Preparation of the Oxime of Ethylic Acetoacetate and its Derivatives.** By ROBERT SCHIFF (*Ber.*, 1895, **28**, 2731—2734).—Ethylic acetoacetate and aniline are dissolved at the ordinary temperature in concentrated aqueous solution of hydroxylamine hydrochloride (all in molecular proportion); when cool, the solution is extracted with ether, and on evaporating the latter the *oxime* remains as a reddish oil, which slowly changes into a crystalline condensation product melting at 124·5—125°. If, instead of extracting with ether, the solution is saturated with sodium carbonate, acetoacetic anilide oxime, $\text{NOH:CMe·CH}_2\text{·CO·NHPh}$, is formed; it has been recently prepared by Knorr and Reuter (Abstr., 1894, i, 371). Ethylic acetoacetate amphidioxime,  $\begin{matrix}\text{CMe—C·COOEt}\\ \| \qquad \|\\ \text{N·OH N·OH}\end{matrix}$, is obtained by the action of sulphuric acid (30 per cent.) and sodium nitrite on the monoxime; contrary to the statement of Nussberger, it gives, with cupric acetate, a brown coloration and then a brown precipitate.

Ketomethylisoxazolone phenylhydrazone,  $\begin{matrix}\text{CMe:N}\\ |\\ \text{NHPh·N:C - CO}\end{matrix}\!\!>\text{O}$, is prepared by treating the solution of ethylic acetoacetate, aniline, and hydroxylamine hydrochloride, as above, with hydrochloric acid and sodium nitrite (compare Knorr and Reuter, *loc. cit.*). *Benzylidene-ketomethylisoxazolone*,  $\begin{matrix}\text{CMe:N}\\ |\\ \text{CHPh:C—CO}\end{matrix}\!\!>\text{O}$, is obtained by any of the following methods: (1) simple mixing of the oxime and benzaldehyde, (2) saturation of an ethereal solution of the oxime and aldehyde with hydrogen chloride, (3) addition of concentrated hydrochloric acid to a mixture of the oxime and aldehyde, (4) addition of fuming hydrochloric acid to a mixture of the aldehyde and acetoacetic anilide oxime. The first method is the least, the third generally the most, satisfactory. The compound, which is deposited in pale yellow, lustrous crystals, softens at 139°, melts and in part decomposes at 141°, and is extremely stable towards acids, being precipitated unchanged from concentrated sulphuric acid on dilution. It is readily soluble in sodium carbonate solution, in potash, and in ammonia, and, if the solution has not been unduly heated, it is reprecipitated on the addition of an acid; if boiled with ammonia for a short time, however, the compound is completely decomposed, benzaldehyde being regenerated. Its solubility in alkalis suggests that in their presence the

isoxazolone ring is resolved, the acid NOH:CMe·C(CHPh)·COOH being formed.
J. B. T.

**Crystallised Lactic acid of Constant Boiling Point.** By FRIEDRICH KRAFFT and W. A. DŸES (*Ber.*, 1895, **28**, 2589—2597).—This may be obtained by drying the commercial acid—best of sp. gr. 1·16—for a week or two in a (? vacuum) desiccator, and distilling it twice under a pressure of 12·15 mm., obtained by means of the water pump. The distillation flask should have a capacity of 60—80 c.c., and should not be more than half filled; the side tube should be wide and as low in the neck as possible, and the receiver should be kept at a temperature of 90—100° to prevent the condensation of water in it; the liquid is first heated in a water bath at 70° to drive off water, and then the residual acid is distilled as rapidly as possible, being heated by a small, rather smoky flame kept in motion under the flask. The product obtained in this way contains 99—99·5 per cent. of the acid; it boils at about 122° under 14—15 mm., at 119—120° under 13—14 mm., and at 82—85° under 0·5—1 mm. pressure; when cooled, it solidifies to white crystals which melt at about 18°, and it is very hygroscopic.
C. F. B.

**Formation of Carbon Chains: Alkylation of Ethylic Malonate and Acetoacetate.** By CARL A. BISCHOFF (*Ber.*, 1895, **28**, 2616—2631).—The velocity of formation of the alkyl derivatives of ethylic malonate and acetoacetate cannot be deduced simply from the time which elapses before the reacting mixture of ethereal salt, sodium ethoxide, and alkylic iodide, or bromide assumes a neutral reaction, because several other reactions may occur which also lead to a condition of neutrality. Thus, the following may all take place: (1) hydrolysis of the original ethereal salt, (2) hydrolysis of the ethereal salt produced, (3) production of an ether of the alkyl group, (4) elimination of the halogen combined with hydrogen, (5) exchange of the alkyl group of the ethereal salt with that of the iodide added. It is therefore necessary to determine experimentally in each case the amount of the "normal" product obtained. For the purposes of comparison, the author numbers the chain of atoms of the normal product in order, beginning with that carbon atom of the alkyl group which is most remote from the methylene group of the original ethereal salt, and proceeding as shown in the accompanying scheme for ethylic isopropylmalonate,

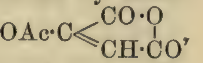


$$\underset{7\ 6\ \ 5\ \ \ 4}{C\cdot C\cdot O\cdot CO}\cdot\underset{3}{\overset{\overset{\overset{1\ 2\ 1}{C\ C\cdot C}}{|}}{C}}\cdot\underset{4\ \ \ 5\ \ 6\ 7}{CO\cdot O\cdot C\cdot C}.$$

The course of the reaction is found to depend on the presence of carbon atoms at the positions 1—5 and 1—6; the more carbon atoms there are in these positions, the less readily does the "normal" reaction proceed. In many cases, moreover, the iodide reacts more readily than the bromide. These results are in agreement with the author's "dynamical theory."

The following are the experimental details. *Derivatives of ethylic malonate;* the numbers express the percentage of the theoretical amount which is experimentally obtained. Methyl-, 70—80 per cent., propyl-, 61—75 per cent.; the bromide gives the better yield; ethyl-, 73—80 per cent.; isopropyl-, 77—85 per cent.; butyl-, about 20 per cent.; isobutyl-, 20—40 per cent.; pseudobutyl-, the "normal" product was not formed either from the chloride or iodide under the usual conditions; traces were produced under a pressure of 5 atmos.; isoamyl-, about 25 per cent.; tertiary amyl-, the "normal" product, was only formed in very small quantity; allyl- good yield. Methylic malonate gives a yield of 75 per cent. of the methyl derivative.

*Derivatives of ethylic acetoacetate:* Methyl-, 76 per cent. from the iodide, 46 per cent. from the bromide; ethyl-, 60 per cent.; propyl-, 72—78 per cent.; isopropyl-, the "normal" product is readily formed from the iodide, but only in traces from the bromide; isobutyl-, 66 per cent. from the iodide, only 6 per cent. from the bromide; pseudobutyl-, the normal reaction does not occur when the chloride is used; isoamyl-, 75 per cent.; tertiary amyl-, the normal reaction does not occur; allyl-, 53—54 per cent. A. H.

**Action of Acetic Anhydride on the Acids of the Acetylene Series.** By Arthur Michael and John E. Bucher (*Ber.*, 1895, **28**, 2511—2512).—Acetylenedicarboxylic acid is converted by acetic anhydride at 100° into *acetoxymaleïc anhydride*,  $OAc\cdot C{<}\begin{matrix}CO\cdot O\\ CH\cdot CO\end{matrix}$, which melts at 89—91°; alcohol converts this into ethylic acetate and oxalacetate, whilst cold water produces the corresponding acids. When ethylic dibromosuccinate, melting at 58°, is treated with sodium ethoxide, the product consists of about 80 per cent. of ethylic *as*-diethoxysuccinate, and 20 per cent. of ethylic ethoxymaleate or ethoxyfumarate. Both of these ethereal salts are converted by hydrolysis into the sodium salt of a *diethoxysuccinic acid*,

$$COOH\cdot CH_2\cdot C(OEt)_2\cdot COOH,$$

which loses the elements of ether when heated at 100° or allowed to stand in a vacuum for some time, oxalacetic acid being formed. The same intermediate product is formed when Nef's ethylic ethoxyfumarate (Abstr., 1893, i, 628) is heated with alcoholic soda.

Phenylpropiolic acid is converted by acetic anhydride into a substance melting at 253°, which has the formula of phenylpropiolic anhydride, but is probably the anhydride of a polymeric dibasic acid. On reduction, this substance is converted into an acid which has the composition of the truxillic acids, but is not identical with any of the acids described by Liebermann. A. H.

**Action of Primary Aromatic Amines on Unsymmetrical Ketonic Compounds.** By Louis Simon (*Bull. Soc. Chim.*, 1895, (3), **13**, 474—484; compare Abstr., 1894, i, 509).—The present instalment of the paper deals with the action of aniline on the alkylic pyruvates, including the ethylic, active amylic, isoamylic, allylic, and benzylic salts; all these substances combine with aniline to form compounds of the type

$$NPh{:}CMe\cdot CO\cdot CH_2\cdot C(COOR){:}NPh,$$

probably by condensation of two molecules of the alkylic anilidopyruvate, in a manner analogous to the condensation of aldehyde-aniline observed by von Miller and Plöchl.

Ethylic pyruvate is readily prepared by boiling the acid with alcohol in a reflux apparatus under ordinary pressure, and fractionating the product under low pressure; the yield is 90 per cent. of that indicated by theory, and the product particularly pure. Ethylic pyruvate is an almost colourless liquid, resembling ethylic acetate in odour, and boiling at 66° (18—20 mm.), and at 155° under the ordinary pressure, in the latter case decomposing slightly; the sp. gr. = 1·080 at 14°; it is freely soluble in water, rapidly becoming hydrolysed into its proximate constituents. The hydrazone is identical with that prepared by Fischer from the hydrazone of pyruvic acid.

The *product* of the condensation of ethylic pyruvate with aniline, $C_{20}H_{20}N_2O_3$, the molecular weight of which was determined by the cryoscopic method, is a white, crystalline solid, melting at 146°; it appears to form two products with phenylhydrazine, a white *substance* melting at 55°, and a yellowish-white *substance* melting at 119—120°. Besides the more complex condensation product, some aniluvitonic acid (methylquinolinecarboxylic acid) is formed at the same time.

Ethylic pyruvate condenses with paratoluidine in a similar manner, a *substance*, $C_{22}H_{24}N_2O_3$, being formed, which crystallises in colourless needles and melts at 186°; at the same time, a second white crystalline substance, melting at 140—143°, is produced.

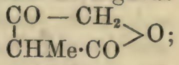
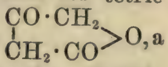
The *condensation product* of aniline with active amylic pyruvate melts at 110—111°, and is unaccompanied by any other product.

*Isoamylic pyruvate* is prepared in the same way as the ethylic salt; it is a limpid, yellowish liquid, having an odour resembling that of amylic acetate, and boiling at 86° (14 mm.), and at about 185° under the ordinary pressure; sp. gr. = 0·978 at 18°. The *phenylhydrazone*, which is very soluble in ether, melts at about 185—186°. The *product* of the condensation of isoamylic pyruvate with aniline, $C_{23}H_{26}N_2O_3$, crystallises in well-defined needles, and melts at 126—127°. The *condensation product* with paratoluidine, $C_{25}H_{30}N_2O_3$, melts at 140°.

*Allylic pyruvate* is prepared by passing hydrogen chloride into a mixture of the acid and the alcohol; it is a colourless liquid, having a pungent odour, and boiling at 65° (14 mm.), and at 165° under the ordinary pressure; sp. gr. = 1·082 at 17·5°. It unites with phenylhydrazine to form a yellow *product* melting at 185°, which does not appear to be the hydrazone. The *condensation product* with aniline, $C_{24}H_{20}N_2O_3$, melts at 136°.

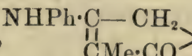
*Benzylic pyruvate* is prepared directly from its proximate constituents; it is a liquid boiling at 103—104° (26 mm.), 107—108° (36 mm.), and at 207—208° under the ordinary pressure; sp. gr. = 1·090 at 14°. The *phenylhydrazone* is a yellow substance melting at 150°. The *condensation product* with aniline, $C_{25}H_{22}N_2O_3$, melts at 173—174°; if kept, however, in the liquid in which it is formed, it is converted into a substance having a higher melting point and containing relatively more carbon.

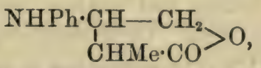
In the preparation of benzylic pyruvate, a liquid is obtained, which, although closely resembling it, forms a compound with phenylhydrazine containing a much larger percentage of carbon than the hydrazone of the benzylic salt. Jn. W.

**Constitution of Tetric (α-Methyltetronic) acid.** By Ludwig Wolff (*Annalen*, 1895, **288**, 1—37; compare Abstr., 1893, i, 689).—The author discusses the structure of tetric acid, which he regards as having the constitution attributed to it by Michael,  $\left.\begin{matrix}\text{CO}-\text{CH}_2\\ \text{CHMe}\cdot\text{CO}\end{matrix}\right>\text{O}$; it is proposed to substitute the name *α-methyltetronic acid* for tetric acid, it being a methyl derivative of tetronic acid,  $\left.\begin{matrix}\text{CO}\cdot\text{CH}_2\\ \text{CH}_2\cdot\text{CO}\end{matrix}\right>\text{O}$, a substance which will be described in a future communication. Pentic acid, therefore, will be called α-ethyltetronic acid.

α-Methyltetronic acid (Demarçay, Abstr., 1880, 625) is obtained by brominating ethylic methylacetoacetate and heating the product for two hours at 120°; when heated with an aqueous solution of barium hydroxide for 30 hours in a reflux apparatus, it yields glycollic and propionic acids, ethylketole being formed at the same time.

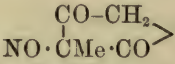
*Ethylketole*, $C_2H_5\cdot CO\cdot CH_2\cdot OH$, is obtained by heating α-methyltetronic acid (10 grams) with water (60 grams) in a sealed tube at 200—210°; it is a neutral, colourless oil which boils at 155—156°, and decomposes slightly under a pressure of 741 mm. It is readily soluble in water, alcohol, and ether, being precipitated from the aqueous solution by salts; the substance reduces Fehling's solution and a silver solution, and is slowly decomposed by alkalis. The *phenylhydrazone* crystallises from petroleum in yellowish prisms, and melts at 76—77°; the *osazone* crystallises in lustrous, yellow prisms, and melts at 116°. Carbonic anhydride and propionic acid are obtained on oxidising α-methyltetronic acid.

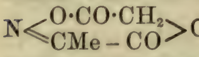
The *anilide* of α-methyltetronic acid,  $\left.\begin{matrix}\text{NHPh}\cdot\text{C}-\text{CH}_2\\ \text{CMe}\cdot\text{CO}\end{matrix}\right>\text{O}$, is obtained by treating the acid with boiling aniline, and pouring the product into water; it crystallises in small, slender needles, and is resolved into its components by boiling, dilute hydrochloric acid. Its *nitroso*-derivative crystallises in yellow needles, and melts and evolves gas at 103—104°.

*α-Methyl-β-anilidobutyrolactone*,  $\left.\begin{matrix}\text{NHPh}\cdot\text{CH}-\text{CH}_2\\ \text{CHMe}\cdot\text{CO}\end{matrix}\right>\text{O}$, is formed when the anilide is reduced with sodium and amylic alcohol; it crystallises from hot water in long needles, and melts at 92°. The aqueous solution is neutral, and indifferent towards boiling dilute hydrochloric acid; Fehling's solution is reduced by it when heated. The *barium* salt of the hydroxy-acid is obtained on treating the lactone with boiling aqueous barium hydroxide.

The author has obtained the bromo-derivative of α-methyltetronic acid in long needles which sinter at 85° and melt at 87—88°; the bromotetric acid prepared by Moscheles and Cornelius melted at 75°. The aqueous solution is feebly acid, and after some time contains hydrobromic acid; when heated at 100°, it yields carbonic anhydride, diacetyl, and methyltetronic acid, a pungent oil which probably consists of bromethylketole being formed at the same time. Bromomethyltetronic acid is immediately dissolved by ammonia and alkalis, and slowly by alkali carbonates, the bromide of the metal being formed; a concentrated aqueous solution of sodium carbonate gives rise to methyltetronic acid and diacetyl.

Methyltetronic acid is readily oxidised, yielding diacetyl, carbonic anhydride, formic and propionic acids, and an oil which closely resembles ethylketole.

*Nitroso-α-methyltetronic acid*,  $\begin{matrix}\mathrm{CO{-}CH_2}\\ \vert\\ \mathrm{NO{\cdot}CMe{\cdot}CO}\end{matrix}\!>\!\mathrm{O}$, is obtained by suspending α-methyltetronic acid in glacial acetic acid, cooling the liquid with ice, and submitting it to the action of a current of gas obtained from arsenious anhydride and nitric acid. On adding water to its solution in acetone, it crystallises out in minute prisms, and melts, evolving gas, at 130—131°; it is indifferent towards cold water and hydrochloric acid, but yields nitrous acid and methyltetronic acid with a small quantity of α-oximidopropionic acid when treated with the boiling agents. Cold aqueous ammonia gives rise to ammonium nitrite, methyltetronic acid, α-oximidopropionamide, and glycollic acid.

*α-Oximidopropionylglycollic acid*, $\mathrm{NOH{:}CMe{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}COOH}$, is obtained when the gas from nitric acid and arsenious anhydride acts on methyltetronic acid in presence of water, and it is prepared in the form of the sodium salt by dissolving the original substance in concentrated aqueous sodium nitrite. It crystallises from water in large, transparent prisms, and undergoes no change at 100°; it melts at 165°, slowly evolving gas, and is occasionally obtained in the form of needles containing water, which effloresce on exposure to air. The *sodium* salt crystallises in lustrous needles containing $1H_2O$; the *silver* salt crystallises in needles which soon become prisms. The *acetyl* derivative crystallises from benzene; it sinters at 102°, and melts at 105°. Cold caustic soda, hydrochloric acid, and boiling water decompose α-oximidopropionylglycollic acid, giving rise to α-oximidopropionic acid and glycollic acid; the amide of the former acid is produced by the action of ammonia, glycollic acid being formed at the same time. α-Oximidopropionylglycollic acid is obtained from nitrosomethyltartronic acid by treating it with boiling solutions of sodium nitrite and sodium acetate, which, however, are without action when cold. The *anhydride*, which may have the constitution  $\mathrm{N}\!<\!\begin{matrix}\mathrm{O{\cdot}CO{\cdot}CH_2}\\ \mathrm{CMe - CO}\end{matrix}\!>\!\mathrm{O}$, is obtained as a bye-product in preparing the acid from α-methyltetronic acid by means of sodium nitrite; it is an amorphous, hygroscopic powder, which begins to decompose at 70°, evolving gas vigorously at 150°. It dissolves readily in alkalis and concentrated acids, and is converted into α-oximidopropionylglycollic acid on treatment with boiling water. M. O. F.

**Dimethylvioluric acid and Dimethyldilituric acid.** By RUDOLF ANDREASCH (*Monatsh.*, **16**, 773—788; compare Abstr., 1895, i, 336).—When dimethylvioluric acid is heated in a water bath with excess of potash, and the product acidified with acetic acid, carbonic anhydride, methylamine, and oximidomalonic acid are formed. If barium hydroxide solution be substituted for the potash, carbonic anhydride and *oximidodimethylmalonamide*, $HO·N:C(CO·NHMe)_2$, are obtained. The latter crystallises from water and from alcohol in needles, and melts at 228° (uncorr.).

Nitrodimethylbarbituric acid, if boiled with baryta water, or allowed to remain in contact with potash for several days, yields *nitrodimethylmalonamide*, $NO_2·CH(COOH_2)_2$, which crystallises from hot water in needles, melts at 156° (uncorr.), and yields a *barium salt*, $(C_5H_8N_3O_4)_2Ba + H_2O$, which crystallises in drusy masses of prisms, a *potassium salt*, which crystallises in white needles, and a *copper salt*, which is soluble in water, and crystallises in sky-blue octahedra. Nitrodimethylmalonamide, when heated with hydrochloric acid in sealed tubes at 110°, yields formic acid, carbonic anhydride, hydroxylamine, and methylamine. An aqueous solution is converted by chlorine and bromine into *chloronitrodimethylmalonamide* and *bromonitrodimethylmalonamide* respectively; the former crystallises in spear shaped needles and melts at 109° (uncorr.), the latter forms four-sided plates and melts at 137—138° (uncorr.). These compounds do not yield salts, the halogen having become attached to the carbon atom bearing the nitro-group. Nitrodimethylbarbituric acid forms similarly constituted compounds when treated with chlorine water and bromine water respectively. *Chloronitrodimethylbarbituric acid*,

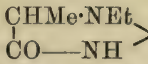
$$NO_3·CCl:(CO·NMe)_2:CO,$$

thus obtained, crystallises from chloroform in slender needles, and from alcohol in octahedra, and decomposes at 150°. *Bromonitrodimethylbarbituric acid*, $C_6H_6BrN_3O_5$, closely resembles the corresponding chloro-compound, turns yellow at 149°, and melts partially at 152°.

G. T. M.

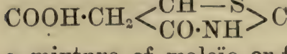
**Methylethylhydantoïn (Ethylpropiohydantoïn).** By Edouard Duvillier (*Bull. Soc. Chim.*, 1895, [3], **13**, 487—490).—When carbamide is heated with α-ethylamidopropionic acid,

$$NHEt·CHMe·COOH,$$

methylethylhydantoïn (ethyllactylcarbamide),  $\begin{matrix}\text{CHMe·NEt}\\ | \\ \text{CO——NH}\end{matrix}\!>\!\text{CO}$, is formed, the hydantoic acid appearing to condense at once to the lactam.

*Methylethylhydantoïn* crystallises in transparent, rhomboidal plates, and is very deliquescent; it is stable towards boiling baryta water, so that the corresponding hydantoic acid cannot be formed by the action of this agent; the lactam is also formed instead of the acid by the action of potassium cyanate on ethylamidopropionic acid.

It thus appears that this hydantoic acid is as unstable as the corresponding creatine, a ring compound being formed in both cases where an open chain compound might be expected. Jn. W.

**Thiohydantoïn.** By Rudolf Andreasch (*Monatsh.*, 1895, **16**, 789—797; compare Abstr., 1888, 47).—*Thiohydantoïnacetic acid*,  $\text{COOH·CH}_2\!<\!\begin{matrix}\text{CH — S}\\ \text{CO·NH}\end{matrix}\!>\!\text{C:NH}$, is obtained on heating together at 105°, a mixture of maleïc or fumaric acid (5 grams), thiocarbamide (3·3 grams), and water (4 c.c.). It is sparingly soluble in cold water, does not dissolve in alcohol, and has a powerful acid reaction (compare Tambach, Abstr., 1895, i, 13). When boiled with barium hydroxide, the acid is resolved into thiomalic acid, and probably cyanamide, although this was not identified, since from these two substances thiohydantoïnacetic acid can be directly synthesised. On oxidation with barium chlorate in hydrochloric acid solution, thiohydantoïnacetic acid yields carbamide and hydrothiosuccinic acid,

$$COOH{\cdot}CH_2{\cdot}CH(SH){\cdot}COOH.$$

*Diphenylthiohydantoïnacetic acid*, obtained on heating a mixture of diphenylthiocarbamide and maleïc acid for $1\frac{1}{2}$—2 hours at 140—144°, crystallises from alcohol in yellowish, nodular masses, and melts at 188° (compare Tambach, *loc. cit.*). G. T. M.

**Formation of 1 : 3 : 5-Trinitrobenzene and 1 : 4-Nitrophenol from Nitromalonic Aldehyde.** By Henry B. Hill and Joseph Torray (*Ber.*, 1895, **28**, 2597—2599).—The sodium derivative of nitromalonic aldehyde, $NO_2{\cdot}CNa(CHO)_2$, is formed when sodium nitrite acts on mucobromic acid. When its aqueous solution is treated with an equivalent quantity of hydrochloric acid and warmed, or simply allowed to remain, 1 : 3 : 5-trinitrobenzene and formic acid are formed. If its aqueous solution is treated with acetone (1 mol.), and soda is gradually added, 1 : 4-nitrophenol is formed. C. F. B.

**Preparation of Parethyltoluene and its Derivatives.** By George Defren (*Ber.*, 1895, **28**, 2648—2653).—The author has attempted to separate the mixture of ethyltoluenes, obtained by the action of ethylic chloride on toluene in the presence of aluminium chloride, by a method similar to that used for the separation of the xylenes (*Zeit. anal. Chem.*, **32**, 243), but as it did not give good results he prepared parethyltoluene by Fittig's synthetical method, and obtained the following derivatives.

*Parethyltoluenesulphonic acid*, $C_6H_3MeEt{\cdot}SO_3H + 1\frac{1}{2}H_2O$, forms glistening plates, melts at 59—60°, and is readily soluble in water. The *barium salt*, $(C_6H_3MeEt{\cdot}SO_3)_2Ba + 2H_2O$, crystallises from water in slender needles, and in the anhydrous form is insoluble in ether and in alcohol; the *sodium salt* crystallises with $1\frac{1}{2}$ $H_2O$; the *sulphonic chloride* is a yellowish, heavy oil, which solidifies when placed in a freezing mixture, and melts at 3°; the *sulphonamide* is readily soluble in ether and in alcohol.

*Parethyltoluonitrile*, obtained by heating dry sodium ethyltoluenesulphonate with potassium cyanide, is a yellowish oil; it begins to boil at 235°, but then rapidly undergoes decomposition, and cannot be hydrolysed by heating with concentrated hydrochloric acid at 200°.

*Chloroparethyltoluene*, obtained by chlorinating the hydrocarbon in the presence of iodine, is an oily liquid with an agreeable odour, and boils at 200° to 203°; on further chlorination, it yields the *dichloro-derivative*, which boils at 240—243°.

*Orthobromoparethyltoluene*, obtained by the action of bromine on the hydrocarbon in presence of iodine, boils at 220—222° (corr.), at the same time undergoing slight decomposition; the *dibromo*-derivative [Me : Et : $Br_2$ = 1 : 4 : 2 ?] boils at 260—265° (uncorr.).

*Chloroparethyltoluenesulphonic acid* crystallises in glistening plates, which readily liquefy when exposed to the air. The *barium* salt crystallises with $4H_2O$, the *sodium* salt is anhydrous, and the *sulphonic chloride* is a yellow oil which does not become solid at −15°.

*Orthobromoparethyltoluenesulphonic acid* crystallises in thin plates, yields a *barium salt*, $(C_6H_2MeEtBr{\cdot}SO_3)_2Ba + 5H_2O$, a *sodium salt*, $C_6H_2MeEtBr{\cdot}SO_3Na + H_2O$, an oily *sulphonic chloride*, and a *sulphonamide* which melts at 143°. J. J. S.

**Three Octochlorophenols.** By ÉTIENNE BARRAL (*Bull. Soc. Chim.*, 1895, [3], **13**, 490—492).—Hexachlorophenol dichloride is the final product of the action of chlorine on phenol in presence of antimonic chloride, and exists in three modifications. The dark brown crystalline product is washed with dilute acid, and recrystallised alternately from light petroleum and chloroform, yielding ultimately a white, crystalline mixture of the three isomerides, melting somewhat indefinitely at 68—70°. The separation is effected by hand, large and sufficiently characteristic crystals of the three varieties being obtained by slow evaporation of the ethereal solution in the cold.

*α-Hexachlorophenol dichloride*, $C_6Cl_8O$, obtained in this manner is identical with that prepared by Benedikt and Schmidt by chlorinating pentachlorophenol in acetic acid solution, and it is also prepared by heating hexachlorophenol in sealed vessels at above 210°, or at a somewhat lower temperature in presence of bromine; it crystallises in orthorhombic prisms, and melts at 103·5—104°.

*β-Hexachlorophenol dichloride* crystallises in flat, orthorhombic prisms, and melts at 89·5—90°. It is converted by fuming sulphuric acid into a *hexachloroquinone*, which has a slight odour of camphor and melts at 87·5—88·5°; this ketone is distinct from that of Zincke and Fuchs, and is converted by phosphorus pentachloride into hexachlorophenol and hexachlorobenzene dichlorides.

*γ-Hexachlorophenol dichloride* crystallises in monoclinic prisms, as broad as they are long, and melts at 88—89°.

The hexachlorophenol dichlorides are reduced to pentachlorophenol by tin and hydrochloric acid, and are converted into the acetate of that substance by acetic anhydride; they are decomposed at temperatures somewhat above their melting points, into chlorine and products containing perchlorodioxyphenylene, but, on the whole, are much more stable than hexachlorophenol, of which they are probably additive derivatives. JN. W.

**Formanilide and its Derivatives.** By LUDWIG CLAISEN (*Annalen*, 1895, **287**, 360—371).—On a former occasion (Abstr., 1895, i, 62), the author traced an analogy between hydroxymethylene compounds, and formanilide, which he represented as hydroxymethyleneaniline, NPh:CH·OH, and this view has been accepted by Auwers (Abstr., 1895, ii, 41; compare also 1894, ii, 133) on the ground that in cryoscopic behaviour formyl derivatives of primary bases differ from those of secondary bases. The author, however, no longer advocates his former conception of the constitution of formanilide on account of the fact that, unlike the sodium derivatives of hydroxymethylene compounds, sodium formanilide does not yield an alkyl ether when treated with alkylic iodides; moreover, whilst hydroxymethylene compounds boil at a lower temperature than their alkyl ethers, formanilide (b. p. 294°) boils 82° higher than the ethyl ether.

Detailed directions for preparing ethylformanilide (*ethoxymethyleneaniline*) from aniline and ethylic orthoformate are to be found in the original paper (compare Comstock and Clapp, Abstr., 1892, 708). In preparing diphenylformamidine (*methenylbisaniline*), there is no occasion to heat aniline with ethylic orthoformate in a sealed tube, as stated by Wichelhaus (*Ber.*, 1869, **2**, 116), the most convenient method being that adopted in preparing the foregoing substance, using the calculated quantities of material.

When phenylhydrazine, dissolved in glacial acetic acid, is brought into contact with ethylic orthoformate at 0°, formylphenylhydrazide and formazylhydride (Abstr., 1893, i, 83) are produced, the yield of the latter substance being larger than when ethylic formate is employed.

Sodium formanilide is conveniently prepared by heating in a reflux apparatus an ethereal solution of aniline containing sodium, and slowly adding the calculated amount of ethylic formate. Formylphenylhydrazide is obtained by heating sodium (23 grams), dissolved in alcohol (500 grams) with phenylhydrazine (108 grams) and ethylic formate (75 grams) for half an hour on the water bath; one-third of the alcohol is distilled off, and the clear liquid obtained on pouring the residue on to melting ice is acidified with dilute acetic acid, when formylphenylhydrazide (108 grams) separates. M. O. F.

**Diázoperhaloïds.** By Arthur R. Hantzsch (*Ber.*, 1895, **28**, 2754—2763).—Nine of the 10 theoretically possible diazoperhaloïds $RN_2X_3$ can readily be obtained (R = an aromatic radicle; X = a haloïd atom); attempts to prepare the trichloride have hitherto failed. These compounds are probably constituted according to the diazonium type $N⋮NRX_3$; they closely resemble the alkali trihaloïds, such as $KI_3$, $CsBr_3$, $H_4NI_3$, &c., of which, in the case of the cæsium derivatives, eight of the 10 possible are known, the trichloride and the chlorodiiodide not having been described. The resemblance extends to the colours: the diazotriiodides are bluish-black, have a metallic lustre, and are almost opaque; the diiodobromides are dark reddish-brown, the dibromiodides cherry-coloured, the tribromides orange, and the chlorobromiodides dark yellow; the remaining compounds are less intensely coloured, the dichlorobromides being pale yellow. The colour is also influenced by the presence of substituting groups in the benzene nucleus. The compounds are unstable, but less explosive than the diazonium monohaloïds; they are sparingly soluble in water, and generally a portion is decomposed; this property being most marked in the case of the two diiodides, the dibrom- and dichlor-iodides and the chlorobromiodide are much more stable. Alcohol dissolves them more readily, and less decomposition takes place; in ether, they scarcely dissolve, and undergo slow decomposition.

Diazoparachlorobenzene cyanide, by the action of bromine, is converted, not into the additive compound $C_6H_4Cl\cdot NBr\cdot NBr\cdot CN$, but into the tribromide, which is also formed from parachlorobenzenediazonium chloride; this does not readily accord with the usual diazo-formula. All attempts, by varying the experimental conditions, to prepare structural isomerides, such as $PhNBr\cdot NClI$ and $PhNCl\cdot NIBr$, or $\begin{matrix}Ph\cdot N\cdot Br\\ | \\ I\cdot N\cdot Cl\end{matrix}$ and $\begin{matrix}Ph\cdot N\cdot Cl\\ | \\ Br\cdot N\cdot I\end{matrix}$ respectively, have been unsuccessful, it is possible that the diazonium radicle $N{\vdots}NPh$— is linked to the trihaloïd group as a whole rather than to any single atom; this would be similar to the hydrogen-nitrogen linking in the imide group of pyrazole, tetrazole, and probably azoimide. Attempts to eliminate selected haloïd atoms from the above compounds, particularly in the absence of solvents which could cause dissociation, were unsuccessful. No pentahaloïds corresponding with $CsX_5$ could be isolated, but evidence of their probable existence is afforded by the fact that all the trihaloïds combine with bromine, iodine, bromine iodide, and chlorine iodide and triiodide to form dark coloured unstable oils. The haloïds may be employed in considerable excess without the benzene nucleus being attacked; this is in marked contrast with aniline and its derivatives; dimethylaniline rapidly attacks bromine water; trimethylphenylammonium salts, like the diazonium salts, are without action; this also favours the diazonium constitution. Most of the diazoiodides are unstable, and are possibly syn-derivatives. *Diazomesitylene iodide*, which will be described later, is exceptional in this respect, and, with alcoholic solution of iodine, yields *mesityldiazonium triiodide*, $C_6H_2Me_3N_2I_3$, which crystallises in dark brown needles with a blue reflex, and decomposes at about 70°.

*Benzenediazonium chlorodiiodide*, $PhN_2ClI_2$, prepared from the diazonium chloride and alcoholic iodine solution in molecular proportion, crystallises in dark violet, lustrous needles, melts at 67°, is stable in dry air, but is quantitatively decomposed by water. The *dichloriodide*, $PhN_2Cl_2I$, is formed by the action of alcohol on the preceding compound and subsequent precipitation with ether; the action takes place in two stages, a portion of the diiodide is resolved into iodobenzene, nitrogen, and iodine chloride, this then combines with the remaining diiodide forming iodine and the dichloriodide; the latter is also formed from benzenediazonium chloride and chloriodide, it is stable, crystallises from alcohol in yellow plates, and melts at 86—87°. The *bromodiiodide*, $PhN_2BrI_2$, is prepared like the preceding compounds, and crystallises in lustrous, brownish-red needles. The *dibromiodide*, $PhN_2Br_2I$, is obtained in a similar manner to the dichloro-derivative, and also from benzenediazonium tribromide and iodine; it forms brown crystals, and decomposes at 77°. The *chlorodibromide*, $PhN_2ClBr_2$, prepared by the action of benzenediazonium chloride and bromine in chloroform solution, is a reddish-yellow, crystalline powder; it melts at 61°, and is comparatively unstable. The *bromodichloride*, $PhN_2BrCl_2$, is formed by the action of chlorine on the tribromide in chloroform solution; it crystallises from alcohol in pale yellow needles, melts at 63°, and is immediately decomposed by water. The *chlorobromiodide*, $PhN_2ClBrI$, is formed from the diazonium chloride or bromide by the action of bromine iodide and chlorine iodide respectively; it is deposited in golden needles melting at 80—81°.

*Parabromobenzenediazonium bromodiiodide*, $C_6H_4Br{\cdot}N_2BrI_2$, can only be prepared at about −15°, and forms brownish-red plates melting at about 79°. The *dibromiodide*, $C_6H_4Br{\cdot}N_2Br_2I$, is obtained, together with parabromiodobenzene, by heating the preceding compound with alcohol or glacial acetic acid, and also from the diazonium bromide and bromine iodide or iodine; it crystallises in brownish-yellow needles, melts and decomposes at 106—107°. The *chlorobromiodide*, $C_6H_4Br{\cdot}N_2ClBrI$, is comparatively stable, and crystallises in golden needles melting at 111—112°.

The paranitrobenzenediazonium trihaloïds are much less stable than the above compounds; attempts to prepare the chlorodiiodide were unsuccessful, as even at very low temperatures nitrogen is evolved and paranitroiodobenzene is formed. *Paranitrobenzenediazonium dichloriodide*, $NO_2{\cdot}C_6H_4{\cdot}N_2Cl_2I$, melts and decomposes at 106°. The *chlorobromiodide*, $NO_2{\cdot}C_6H_4{\cdot}N_2ClBrI$, forms yellow crystals, melts at 93°, and, with alcohol, yields bromoparanitrobenzene. J. B. T.

**β-Lactylphenylhydrazide: Phenylhydrazine Citrate and Tartrate.** By HENRY J. F. DE VRIES (*Ber.*, 1895, **28**, 2611—2612).—*β-Lactylphenylhydrazide*, $NHPh{\cdot}NH{\cdot}CO{\cdot}CHMe{\cdot}OH$, is formed when phenylhydrazine and lactic acid are heated together at 130—140°; it forms white crystals, which melt at 114·5°. *Phenylhydrazine citrate* melts at 102°. *Phenylhydrazine d-tartrate* probably has the formula, $(N_2H_3Ph)_2C_4H_6O_6 + 3H_2O$, and turns brown in the air. A. H.

**Phenylazocarboxylamide and Phenylazocarboxylic acid.** By JOHANNES THIELE (*Ber.*, 1895, **28**, 2599—2601).—Phenylazocarboxylamide, $NPh{:}N{\cdot}CONH_2$ (Widman, Abstr., 1895, i, 603), when it is formed in presence of water, crystallises with $2H_2O$ as an orange-yellow powder that melts at 84°; it readily loses its water by deliquescence, or when recrystallised from organic solvents, and then forms red needles melting at 114°. Its (mono-) *potassium derivative* forms dark red plates. *Potassium phenylazocarboxylate*, $NPh{:}N{\cdot}COOK$, is obtained by the action of potash on phenylazocarboxylamide, or by the oxidation of phenylsemicarbazide in alkaline solution; it crystallises in orange-red needles, and is decomposed by water.

*β-Naphthylazocarboxylamide* is obtained, though much less easily than the phenyl compound, by the oxidation of β-naphthylsemicarbazide; it forms orange-red crystals, and melts at 137—138°.

C. F. B.

**Ketones from Propenyl Compounds.** By OTTO WALLACH and F. J. POND (*Ber.*, 1895, **28**, 2714—2722).—If anethoïl is converted into the dibromide, and the latter treated with sodium methoxide, an oil is formed which contains the compound, $OMe{\cdot}C_6H_4{\cdot}C(OMe){:}CHMe$;

if the crude product of the action is distilled with steam, *ethyl anisyl ketone*, $OMe\cdot C_6H_4\cdot CO\cdot CH_2Me$, is obtained; this melts at 26—27°, and boils at 136—139° under 12 mm. pressure, at 265—270° under atmospheric pressure; the *oxime* melts at 74°, the *semicarbazone* at 172—173°. When oxidised with permanganate, the ketone yields anisic acid and a ketonic acid, $OMe\cdot C_6H_4\cdot CO\cdot COOH$, which melts at 75°, and is very soluble in water. When it is heated with strong sulphuric acid at 200°, some propionic acid is formed.

Isosafrole, $CH_2{:}O_2{:}C_6H_3\cdot CH{:}CHMe$, and ethylisoeugenol,

$$OMe\cdot C_6H_3(OEt)\cdot CH{:}CHMe,$$

behave in exactly the same way, the ketone formed always containing the carbonyl group directly attached to the benzene ring. The *ketone*, $CH_2{:}O_2{:}C_6H_3\cdot CO\cdot CH_2Me$, melts at 39°, and boils at 153—154° under 13 mm. pressure; the *oxime* melts at 104°. It is probably identical with the ketone obtained by Angeli (Abstr., 1892, 1198), and perhaps also with another obtained by Tonnies (Abstr., 1888, 264) from anethoïl nitrite.

The *ketone*, $OMe\cdot C_6H_3(OEt)\cdot CO\cdot CH_2Me$, melts at 62°, and boils at 155° under 13 mm. pressure; the *oxime* melts at 114°, the *semicarbazone* at 175°. When oxidised, it yields two acids, one sparingly soluble in water and melting at 190°, the other (? ketonic) easily soluble, and melting at 64—65°. The ketone is doubtless identical with that obtained by Hell and Portmann (Abstr., 1895, i, 657).

C. F. B.

**Etherification and Hydrolysis.** By RUDOLF WEGSCHEIDER (*Ber.*, 1895, **28**, 2535—2536; compare Abstr., 1895, i, 499).—The author, in reply to Meyer (*Ber.*, 1895, **28**, 1798), maintains his former criticism of Meyer's theory of the etherification of substituted ethereal carboxylates. He also criticises Brühl's treatment (*Ber.*, 1895, **28**, 1913) of the same question. A. H.

**Dinitrobenzoic acids.** By FR. GRELL (*Ber.*, 1895, **28**, 2564—2565).—2 : 5-Dinitrobenzoic acid can be obtained by oxidising with nitric acid at 140—150° the 2 : 5-dinitrotoluene obtained by Sandmeyer's reaction from 5-nitro-orthotoluidine. In the same way, 2 : 3-*dinitrobenzoic acid* can be obtained from 2 : 3-dinitrotoluene, the latter being obtained when 2-acetotoluidide is nitrated, and the resulting 3-nitro-derivative treated with nitrous acid and cuprous oxide; the acid melts at 201°, the *barium salt* crystallises with $4H_2O$.

C. F. B.

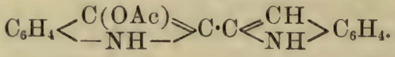
**Isocoumarincarboxylic acid.** By EUGEN BAMBERGER (*Annalen*, 1895, **288**, 134—138; compare Abstr., 1893, i, 592).—In order to establish the identity of the acid obtained by oxidising dihydronaphthol with potassium permanganate (*loc. cit.*), isocoumarincarboxylic acid was reduced with sodium amalgam, the product being identical with dihydroisocoumarincarboxylic acid, as already described.

When isocoumarincarboxylic acid is treated during one hour with boiling, aqueous caustic soda, orthotoluic acid is produced, oxalic acid being formed at the same time. Other ketonic acids undergo analogous decomposition; thus pyruvic acid and phthalonic acid,

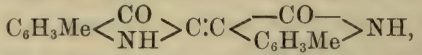
$COOH{\cdot}C_6H_4{\cdot}CO{\cdot}COOH$, yield oxalic acid when treated with boiling, aqueous soda, but benzoylformic acid does not behave in this way.

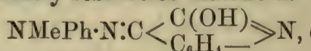
M. O. F.

**The Red Isomeride of Indigotin; Derivatives of Isatin.** By EDWARD SCHUNCK and LEO MARCHLEWSKI (*Ber.*, 1895, **28**, 2525—2531; compare Abstr., 1895, i, 288).—The three substances which have been described as red isomerides of indigotin have been proved by the authors to be identical; this identity is further shown by the fact that they all yield the same substance when treated with zinc dust in presence of acetic anhydride and dehydrated sodium acetate. This product crystallises in faintly pink, lustrous needles melting at 204°. It appears to be *acetylindileucin*,



$$C_6H_4<\substack{C(OAc)\\ -NH-}>C{\cdot}C<\substack{CH\\ NH}>C_6H_4.$$

*Dimethylindirubin*,  $C_6H_3Me<\substack{CO\\ NH}>C{:}C<\substack{-CO-\\ C_6H_3Me}>NH$, is formed by the reduction of paramethylisatin chloride. It crystallises in chocolate-brown needles, and closely resembles indirubin.

*Isatinmethylphenylhydrazone*,  $NMePh{\cdot}N{:}C<\substack{C(OH)\\ C_6H_4-}>N$, crystallises in orange needles melting at 172—173°; it is strictly analogous to isatinphenylhydrazone, and it is, therefore, probable that both of these substances are true hydrazones, and not azo-compounds, since the "mobile" hydrogen of the hydrazone is replaced by methyl in the methylhydrazone. *Isatinacetylmethylphenylhydrazone* forms yellow needles melting at 145°. *Isatin-β-naphthylhydrazone* crystallises in dark yellow needles melting at 234°.

Isatin readily reacts with orthophenylenediamine, *isatohydrophenazine*, $C_{14}H_9N_3$, being obtained; it is as yet doubtful whether this substance is a derivative of isatin or of pseudo-isatin. It crystallises in yellow needles which melt at 285—287°, and can be sublimed; it is stable towards acids and alkalis, and is insoluble in the latter. The *silver salt* is a reddish-brown powder. The *acetyl derivative* melts at 202°.

*Metachlorisatohydrophenazine*, $C_{14}H_8ClN_3$, is prepared from metachlorisatin and orthophenylenediamine, and crystallises in sparingly soluble, yellow needles. Its *silver salt* is an orange coloured precipitate. The *acetyl compound* melts at 215°.

A. H.

**Reduction Products of Azo-compounds.** By PAUL JACOBSON (*Ber.*, 1895, **28**, 2541—2558; compare Abstr., 1895, i, 26).—The main object of the following research was to experimentally determine whether ortho- and meta-methylazobenzene and metazotoluene undergo the normal reaction when converted into benzidine derivatives; all the three compounds were found to yield derivatives of paradiamidodiphenyl. Many of the substances described have already formed the subjects of patents.

I. With W. LISCHKE.—Orthomethylazobenzene is a red oil which boils at 180—181° (corr.) under 20 mm. pressure. The hydrazo-compound melts at 101°. 3-*Methylbenzidine* [$Me : (NH_2)_2 = 3 : 4 : 4'$] is a syrup which could not be obtained crystallised. Its *dibenzylidene derivative*, $CHPh\dot{:}N{\cdot}C_6H_4{\cdot}C_6H_3Me{\cdot}N\dot{:}CHPh$, forms yellowish tablets melting at 134°.

4 : 4'-*Diiodo*-3-*methyldiphenyl*, $C_6H_4I{\cdot}C_6H_3MeI$, is obtained by means of the diazo-reaction from methylbenzidine. It forms rosettes of needles, and melts at 109°. When it is distilled with zinc dust, it yields metaphenyltoluene, identical with the hydrocarbon which has been described by Adam (Abstr., 1888, 959). It follows from this, that methylbenzidine has been formed from orthomethylhydrazobenzene in the normal manner.

II. With A. W. Nanninga.—Metamethylazobenzene is usually prepared (German Patent, No. 54,599) by the elimination of the amido-group from the condensation product formed from diazobenzene chloride and orthotoluidine; it may also be obtained by the condensation of metanitrotoluene with aniline in the presence of alkalis. It crystallises in prisms, melts at 18—19°, boils at 175° (pressure = 19 mm.), and has the sp. gr. 1·065 at 20°/4°.

*Metamethylhydrazobenzene*, $NHPh{\cdot}NHC_6H_4Me$, crystallises in yellowish needles, and melts at 59—61°.

The corresponding 2-methylbenzidine (4 : 4'-*diamido*-2-*methyldiphenyl*) cannot be obtained in the crystalline form. The *hydrochloride* forms long needles. The *diacetyl* derivative crystallises in pointed prisms which do not melt when heated to 300°. The *dibenzylidene* derivative crystallises in groups of small needles and melts at 111—112°. The *diorthohydroxybenzylidene* derivative,

$$OH{\cdot}C_6H_4{\cdot}CH\dot{:}N{\cdot}C_6H_4{\cdot}C_6H_3Me{\cdot}N\dot{:}CH{\cdot}C_6H_4{\cdot}OH,$$

crystallises in slender prisms which melt indefinitely at about 160°. 4 : 4'-*Diiodo*-2-*methyldiphenyl* forms arborescent crystals melting at 114—116°. 4 : 4'-*Dihydroxy*-2-*methyldiphenyl* crystallises in lustrous plates melting at 155—157°. When the diiodo-derivative is distilled with zinc dust, it yields orthophenyltoluene, identical with the hydrocarbon described by Oddo and Curatolo (Abstr,, 1895, i, 606). The formation of the benzidine compound in this case is, therefore, normal.

III. With O. Fabian.—Metazotoluene, together with some of its derivatives, has already been described by Buchka and Schachtebeck (Abstr., 1889, 701). The *dibenzylidene* derivative of the corresponding tolidine, $C_{12}H_6Me_2(N\dot{:}CHPh)_2$ [$= 2 : 2' : 4 : 4'$], crystallises in stellate groups of light yellow tablets melting at 172—173°. The *diorthohydroxybenzylidene* derivative melts at 198—199°. This tolidine was then converted into the diiodo-derivative, and this, without complete purification, distilled with zinc dust. The hydrocarbon produced is converted by oxidation into diphenic acid, and is therefore orthoditolyl. The conversion of the hydrazo-compound into tolidine has, therefore, also proceeded normally in this case.

IV. With K. Michaelis, and A. W. Nanninga.—2 : 4-*Dimethylazobenzene*, $C_6H_3Me_2{\cdot}N_2Ph$, prepared from metaxylidine and nitrobenzene, boils at 205—215° (pressure = 50 mm.), and has the sp. gr. 1·071 at

20°/4°. The *hydrazo-compound* crystallises in white needles melting at 77—79°.

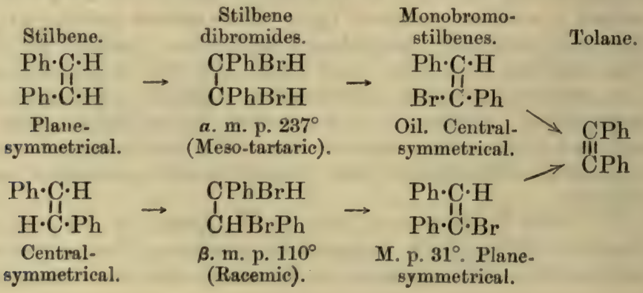
4 : 3′-Dimethylazobenzene, $C_6H_4Me{\cdot}N_2{\cdot}C_6H_4Me$, which has been previously obtained by Zincke and Lawson (Abstr., 1886, 795), may also be prepared from paratoluidine and metanitrotoluene. It crystallises in red needles melting at 55°. The corresponding *hydrazo-compound* crystallises in colourless six-sided tablets and melts at 74°.

A. H.

**Isomeride of Hydroxydiphenylethylamine.** By Henryk G. Söderbaum (*Ber.*, 1895, **28**, 2522—2524).—The author has obtained, in the preparation of hydroxydiphenylethylamine, an isomeric substance which appears to be identical with the compound obtained by Erlenmeyer by the condensation of benzaldehyde with glycocine (Abstr., 1895, i, 596), and by Polonowska by the reduction of benzilemonoxime (Abstr., 1888, 485). It melts at 129°, and forms a *hydrochloride* which at first separates as an amorphous mass, but changes into slender needles. The *platinochloride*, $2C_{14}H_{15}NO,H_2PtCl_6$, is anhydrous, and melts at 213°.

A. H.

**Stilbene Dibromides and Monobromostilbenes.** By Johannes Wislicenus and Felix Seeler (*Ber.*, 1895, **28**, 2693—2703).—When stilbene is treated with bromine in carbon bisulphide solution, two, doubtless geometrically isomeric, dibromides are formed; the less soluble α-compound melts at 237°, the more soluble β-(*iso*)compound at 110—110·5°. The α-compound is always the main product, and so would appear to be the normal additive product of ordinary stilbene, but if that be so, it is remarkable that increase of temperature or of light intensity during the operation causes a larger amount of it to be formed; as a rule the amount of the abnormal product is increased thereby. Either of the two dibromides undergoes a partial conversion into the other when heated. Both yield monobromostilbenes, when treated with alcoholic potash; the α-compound yields an oil, the β-compound crystals melting at 31°. These bromostilbenes both yield tolane when treated with alcoholic potash, but the crystallised compound does this very much more readily than the other, and hence has the hydrogen and bromine atoms in corresponding positions. From this the stereochemical formulæ of the other compounds mentioned can be deduced.



The dibromides are thus represented as derived from isomeric stilbenes; the authors were, however, unable to obtain satisfactory evidence that stilbene does exist in two configurations.

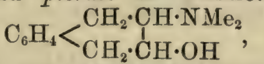
C. F. B.

**Formation of Triphenylcarbinol.** By Hg. Frey (*Ber.*, 1895, **28**, 2514—2521).—Sodium decomposes ethylic oxalate into ethylic carbonate and carbonic oxide. When a solution of ethylic oxalate and bromobenzene in ether is treated with sodium, a mixture of hydrogen and carbonic oxide is evolved and triphenylcarbinol is formed together with benzoic acid. It is probable that the bromobenzene is first converted into benzaldehyde or benzophenone by the carbonic oxide and hydrogen in presence of sodium, and that the triphenylcarbinol is obtained from this. The product actually contains a small amount of benzaldehyde, and both this substance and benzophenone yield triphenylcarbinol when they are mixed with bromobenzene in ethereal solution and treated with sodium. The yield obtained from benzophenone is almost quantitative.

The author has attempted to prepare the corresponding derivative from acetone and methylic iodide, but without success, isopropylic alcohol being the chief product. Parabromaniline, moreover, does not yield pararosaniline when treated with sodium and ethylic oxalate, although nitrogen compounds of high melting point are formed.

A. H.

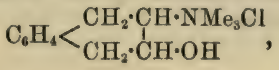
**Alicyclic Derivatives of Naphthalene.** By Eugen Bamberger, and Wilhelm Lodter, [with Bernhard Deicke] (*Annalen*, 1895, **288**, 74—133; compare Abstr., 1893, i, 591, and 1894, i, 419).—The paper contains a detailed account of the preparation and properties of those derivatives which have been already described (*loc. cit.*), and the following facts (obtained in conjunction with B. Deicke) are also recorded.

The *hydrochloride* and *picrate* of 2-dimethylamido-3-hydroxytetrahydronaphthalene,  $C_6H_4<\begin{array}{l}CH_2\cdot CH\cdot NMe_2\\ CH_2\cdot CH\cdot OH\end{array}$, melt at 180—181° and 182° respectively; the *aurochloride* crystallises in lustrous, yellow needles, and the *platinochloride* forms orange-red leaflets. The *methiodide* crystallises from water in long, lustrous prisms, and melts at 201°, and the *benzoate* crystallises in aggregates of needles; the latter has powerful toxic properties.

The *hydrochloride* and *picrate* of 2-diethylamido-3-hydroxytetrahydronaphthalene (diethyltetrahydronaphthylalkine) melt at 167—170° and 170·5—171° respectively; the *aurochloride* crystallises in yellow leaflets or needles, and the *platinochloride* is orange-red. The *methiodide* crystallises in white leaflets and melts at 151·5°, and the *benzoate* separates from alcohol in reddish-yellow, lustrous needles; the latter forms a *picrate* which crystallises in yellow needles.

The *aurochloride* of 2-piperidyl-3-hydroxytetrahydronaphthalene crystallises in yellow leaflets, and the *platinochloride* separates from water in orange-red crystals.

Trimethyl-3-hydroxytetrahydronaphthylammonium chloride,



$$C_6H_4<\begin{array}{l}CH_2\cdot CH\cdot NMe_3Cl\\ CH_2\cdot CH\cdot OH\end{array},$$

forms crystals belonging to the monoclinic system: $a : b : c = 1{\cdot}0854 : 1 : 0{\cdot}5081$; $\beta = 67° 43'$. Precipitates similar to those formed by choline are produced when the chloride is treated with common reagents for the detection of alkaloïds. The *platinochloride* crystallises in orange needles and melts at 222—223·5°; the *aurochloride* separates from water in lustrous, golden-yellow leaflets, and melts at 152—154°. The *picrate* crystallises in flat needles, and melts at 161—162°.

The *hydrochloride* of bishydroxytetrahydronaphthylamine,

$$NH_2(C_{10}H_{10}{\cdot}OH)_2Cl\ [NH : OH = 2 : 3],$$

separates from alcohol on adding ether in lustrous, white needles. The *platinochloride*, which is only sparingly soluble in cold water, crystallises in light-orange needles which melt and decompose at 235°; the *aurichloride* crystallises in lustrous, yellow leaflets.

The *platinochloride* of 2 : 3-hydroxytetrahydronaphthylamine crystallises in reddish-yellow prisms, and the *aurichloride* forms needles. The *picrate* dissolves in hot water, and crystallises in needles.

M. O. F.

**Tetralkyldiamidoazonaphthalenes.** By PAUL COHN (*Monatsh.*, 1895, **16**, 798—806).—*Tetramethyldiamido-α-azonaphthalene* is obtained on passing nitric oxide for two or three weeks through an alcoholic solution of α-dimethylnaphthylamine (compare Lippmann and Fleissner, Abstr., 1883, 55, 184, 868, 1100). It separates from alcohol, in which it is only sparingly soluble, in brownish-red, dichroic crystals, sinters at 140°, and melts at 145°; it yields a yellowish-brown crystalline *picrate*, $C_{24}H_{24}N_4,2C_6H_2(NO_2)_3{\cdot}OH$, which is almost insoluble in boiling organic solvents, and, on reduction with stannous chloride in hydrochloric acid solution, forms paradimethylamidonaphthylamine (compare Friedländer and Welmans, Abstr., 1889, 150).

*Tetrethyldiamido-α-azonaphthalene*, obtained in a similar manner to that employed in preparing the tetramethyl compound, crystallises in reddish-yellow, rhombic plates, gives, with hydrochloric acid, a blue coloration, which is destroyed on the addition of water, and melts at 143° to a reddish-brown liquid; it yields a *picrate*,

$$C_{28}H_{32}N_4,2C_6H_2(NO_2)_3{\cdot}OH,$$

which crystallises in reddish-brown needles, is sparingly dissolved by ordinary solvents, and melts and decomposes at 200°.

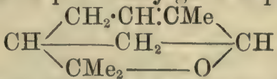
*Dipropyl-α-naphthylamine*, $C_{16}H_{21}N$, obtained on heating a mixture of α-naphthylamine, potash solution, and normal propylic iodide under pressure at 180°, boils at 300°, has a specific gravity of 0·9935 at 20°, yields a *hydrochloride*, $C_{16}H_{21}N,HCl,H_2O$, which crystallises in white needles, a *hydriodide*, $C_{16}H_{21}N,HI$, which crystallises in yellow, felted needles, and a yellow *platinochloride*, $(C_{16}H_{21}N)_2,H_2PtCl_6$, which darkens at 160°, and melts and decomposes at 212°. No definite azo-compound could be obtained by the action of nitric oxide on dipropyl-α-naphthylamine. G. T. M.

**Terpenes and Ethereal Oils. Phellandrene.** By OTTO WALLACH and AD. HERBIG (*Annalen*, 1895, **287**, 371—384; compare Abstr., 1887, 965; 1888, 1204).—The result of the author's investigation shows that reduction of phellandrene nitrite gives rise to optically active tetrahydrocarvone, tetrahydrocarveole, and tetrahydrocarvylamine, the inactive modifications of which have been already described (Abstr., 1894, i, 44) as arising from carvenone (Abstr., 1895, i, 622), on reducing it with sodium and alcohol; on preparing racemic mixtures of the compounds from *d*- and *l*-phellandrene, inactive tetrahydro-derivatives of the carvone series are obtained.

Phellandrene nitrite, which melts at 105°, is prepared in the following manner; 100 grams of hydrocarbon, rich in phellandrene, are placed in a beaker surrounded by a freezing mixture, along with 400 grams of petroleum, and covered with dilute sulphuric acid, prepared by mixing 37 grams of the concentrated acid with twice its volume of water; 230 grams of a 44 per cent. solution of sodium nitrite is then slowly added, the temperature being maintained below 4°, and the liquid gently stirred from time to time. Eucalyptus oil was employed as the source of *l*-phellandrene, bitter fennel oil being used when derivatives of *d*-phellandrene were required.

When phellandrene nitrite is treated with alcoholic sodium ethoxide, it becomes red, heat being generated and nitrous oxide liberated; in this way, a pale yellow oil is obtained, which boils at 134—138°, and has a penetrating odour; it is identical with the "nitrophellandrene" described by Pesci (Abstr., 1886, 1038). On reducing phellandrene nitrite, or the foregoing compound dissolved in absolute alcohol, with sodium, the ketone, $C_{10}H_{18}O$, the alcohol $C_{10}H_{20}O$, and the base $C_{10}H_{19}\cdot NH_2$, are obtained. The ketone boils at 90—100° under a pressure of 15 mm., and yields a dextrorotatory *oxime*, which crystallises in needles, and melts at 97—98°; the *semicarbazone* melts at 185—187°. The alcohol (tetrahydrocarveole) is obtained on reducing the ketone with sodium and alcohol; it boils at 100—104° under a pressure of 12 mm. The base (*tetrahydrocarvylamine*, Abstr., 1894, i, 44) boils at 210—212°, and absorbs carbonic anhydride. The *hydrochloride* melts at 199—204°, and the *acetyl* derivative at 158—159°; the *carbamide* and *phenylcarbamide* melt at 201—203° and 185—186° respectively. When sodium nitrite is added to a feebly acid solution of the hydrochloride, the alcohol is produced, and this substance, on oxidation, yields the ketone.

The authors discuss the constitution of phellandrene. M. O. F.

**Pinole.** By OTTO WALLACH (*Ber.*, 1895, **28**, 2708—2713).—The author has modified the formula he previously gave to pinole (Abstr., 1895, i, 59), and now regards  $CH\left\langle\begin{array}{l}CH_2\cdot CH{:}CMe\\ \text{———}CH_2\text{———}\\ CMe_2\text{———}O\end{array}\right\rangle CH$ as the most probable, although it does not satisfactorily explain all the reactions; in deducing it, regard was had to the fact that terpineole appears to have an hydroxyl group in a side chain.

If pinole glycol is prepared from pinole by direct oxidation, and also by means of the dibromide of the latter, the properties of the two samples are not quite identical.

The ketone, $C_{10}H_{16}O$, prepared by reducing pinole tribromide (*loc. cit.*) in acid solution, has been obtained pure by means of its semicarbazone; it boils at 214—217°; at 20° its sp. gr. = 0·916, and index of refraction $n_D = 1·46603$; the semicarbazone melts at 158°; the oxime boils at 150° under 15 mm. pressure, and can be reduced to a base $C_{10}H_{17}·NH_2$, the hydrochloride of which can be transformed into a carbamide, $C_{10}H_{17}·NH·CO·NH_2$, melting at 186°. The ketone probably contains one ethylene linking, possibly in a side chain in which it is probable that the oxygen atom also is contained. The alcohol, $C_{10}H_{18}O$, obtained by reducing the pure ketone, boils at 108° under 15 mm. pressure, has sp. gr. = 0·913, and index of refraction $n_D = 1·47292$ at 18°. If pinole tribromide is treated with silver acetate in the cold, a compound, $C_{10}H_{17}Br_2O·OAc$ is formed; if heat is employed, an acetate containing no bromine is obtained, the semicarbazone of which melts at 177—178°. C. F. B.

**Oxidation Products of Dihydrocarvone.** By OTTO WALLACH (*Ber.*, 1895, **28**, 2703—2707).—When dihydrocarvone is oxidised, two ketones are formed, in addition to various acids, including oxalic acid and an acid that melts at 203—204°, and contains 59·43 and 8·38 per cent. of carbon and hydrogen respectively. The ketone formed in larger quantity melts at 115—120°, and boils at about 200° under 100 mm. pressure; it is a *ketoglycol*, $C_{10}H_{18}O_3$, the *oxime* of which, $C_{10}H_{18}O_2{:}NOH$, melts at 202°, and the *semicarbazone* at 187°; when boiled for a long time with dilute sulphuric acid, it yields a *ketone*, boiling at 220°, the *semicarbazone* of which melts at 206°. The second of the two original ketones boils at about 130° under 10 mm. pressure, and solidifies in a freezing mixture; it is a *diketone*, $C_9H_{14}O_2$; its *oxime* and *semicarbazone* melt at 195° and 203—204° respectively; it can be obtained from the ketoglycol by further oxidation. C. F. B.

**Camphoronic acid.** By ARNOLD HESS (*Ber.*, 1895, **28**, 2687—2693).—Pure camphoronic acid, $C_9H_{14}O_6$, melts at 148—150° when it is placed in a bath at 136°, and the latter rapidly heated. When it is slowly heated, starting from the ordinary temperature, it is converted for the most part into the anhydride.

It yields a *triethylic*, together with the diethylic, *salt* when its solution in absolute alcohol is saturated with gaseous hydrogen chloride; it boils at 295—300°.

When the diethylic salt is treated with alcoholic ammonia, it yields ammonium ethylic camphoronamate,

$$NH_2·CO·C_6H_{11}(COOEt)·COONH_4,$$

melting at 144—145°; this can also be obtained by the action of ammonia on ethylic anhydrocamphoronate, $O{:}C_2O_2{:}C_6H_{11}·COOEt$. When boiled with aqueous alkalis, it yields *camphoronimic acid*, $NH{:}C_2O_2{:}C_6H_{11}·COOH$, melting at 210°. When the above-mentioned diethylic salt is heated at 120—130° with alcoholic ammonia, or when a benzene solution of anhydrocamphoronic acid is saturated with ammonia and then heated at 140°, ammonium camphoronimate, $NH{:}C_2O_2{:}C_6H_{11}·COONH_4$, melting at 175°, is formed; this only loses half of its nitrogen when boiled with aqueous alkalis. By heating triethylic camphoronate with alcoholic ammonia at 170—190°, a few crystals, melting at 210—218°, were obtained; these were possibly camphoronimic amide, $NH:C_2O_2:C_6H_{11}\cdot CONH_2$. C. F. B.

**Compounds from Lichens. Atranoric acid and Substances accompanying it.** By WILHELM ZOPF (*Annalen*, 1895, **288**, 38—74; compare Abstr., 1895, i, 297).—Atranoric acid is the substance first isolated from *Lecanora atra* (Hudson) by Paternò and Oglialoro (this Journal, 1877, ii, 986); its presence in *Cladonia rangiformis* (Schaerer) and *Stereocaulon vesuvianum* (Pers.) has been since observed by Paternò, and its existence in the dissimilar groups, to which the first-named lichen and the last two belong, has led the author to conduct a systematic search for atranoric acid among 33 different varieties. The investigation has revealed the presence of this acid in the lichens *Stereocaulon alpinum* (Laurer), *S. coralloïdes* (Fries), *S. incrustatum* (Flörke), *S. denudatum* (Flörke), *var. genuinum* (Fries), *S. tomentosum* (Fries), *S. pileatum* (Acharius), *S. condensatum* (Hoffmann), *S. paschale* (L. and Fries), *S. virgatum* (Ach.), *forma primaria* (Wainio), *S. ramulosum* (Ach.), *Physcia cæsia* (Hoffmann), *P. pulverulenta* (Schreber), *var. β-pityrea* (Ach.), *P. endococcina* (Körber), *P. tenella* (Ach.), *P. aipolia* (Ach.), *Anaptychia ciliaris* (L.), *A. speciosa* (Wulf), *Parmelia encausta* (Sommerfelt), *P. pertusa* (Schrk.), *Parmeliopsis hyperopta* (Ach. and Nyl.), *Hæmatomma coccineum* (Dickson), *Placodium saxicolum* (Poll.), and *P. melanaspis* (Ach. and Fries), in addition to those already mentioned.

The cortex of the thallus is stained yellow by alkalis in the case of those species which contain an appreciable amount of atranoric acid, the coloration being very feeble when the acid is present in small quantity; the test, however, is not trustworthy, as a yellow stain with alkalis may arise from the presence of evernic or thamnolic acids. The lichens *Hæmatomma ventosum* (L.), *Placodium radiosum* (Hoffmann), *Cladonia cornuta* (Ach.), *C. gracilis* (L.) *forma chordalis* (Flörke), *C. g.*, *forma aspera*, *C. macilenta* (Ehrb.), *C. furcata* (Hudson) *forma polyphylla* (Flörke), and *C. squamosa* (Hoffmann), do not contain atranoric acid, and *Placodium crassum* (Hudson), identical with *Psoroma crassum*, *var. cæspitosum* (Schaerer), contains only a trace of it.

Atranoric acid, $C_{19}H_{18}O_8$, has been already described by Paternò and Oglialoro (*loc. cit.*); it separates from chloroform in crystals several millimetres in length, and melts at 195—197°. The crystals belong to the rhombic system; $a : b : c = 0\cdot7773 : 1 : 1\cdot2808$. Atranoric acid yields with alkalis a yellow solution, from which it is precipitated by carbonic anhydride; a yellow coloration is developed on dissolving the substance in concentrated sulphuric acid, and the alcoholic solution becomes purple-red with ferric chloride.

*Hæmatommic acid*, $C_{11}H_{12}O_5$, is obtained by heating atranoric acid (1 gram) with absolute alcohol (40 c.c.) in a sealed tube at 150° for one hour; it crystallises from dilute alcohol in snow-white, silky needles, and melts at 113—114°. It is exceedingly soluble in hot alcohol, and also dissolves in cold ether, chloroform, and benzene, whilst cold alcohol and light petroleum dissolve it but sparingly; the substance dissolves in alkalis and alkali carbonates, forming a yellow solution, from which it is precipitated by carbonic anhydride, and the alcoholic solution develops a purple-brown coloration with ferric chloride. When an alcoholic solution of atranoric acid is boiled for many hours in a reflux apparatus, hæmatommic acid is produced; it is, therefore, undesirable to employ boiling alcohol in recrystallising atranoric acid, and prolonged treatment of the lichens with boiling alcohol is to be avoided. Hæmatommic acid has been isolated from the lichens *Hœmatomma coccineum* and *Physcia cœsia.*

*Hœmatommenic acid*, $C_{21}H_{22}O_{10}$, is obtained by heating atranoric acid (9·5 grams) with methylic alcohol (20 c.c.) in a sealed tube at 150° for one hour; it crystallises from a mixture of methylic alcohol and chloroform in thread-like aggregates of colourless needles, and melts at 146—147°. The solution in alkalis and alkali carbonates is yellowish-green, and the acid is precipitated by carbonic anhydride.

*Ommatic acid* is formed when atranoric acid is heated with propylic alcohol in a sealed tube at 150° for one hour; it melts at 75°, and dissolves in alkalis and alkali carbonates, forming a yellow solution.

In addition to the lichens already mentioned (Abstr., 1895, i, 298), *Lecanora* (*Zeora*) *sordida*, *Hœmatomma coccineum*, and *Placodium saxicolum* contain zeorin, which crystallises from chloroform or absolute alcohol in hexagonal double pyramids; it melts at 247—252°, and is insoluble in hot alkalis. When treated with boiling alcohol and hydrochloric acid, it yields *zeorinin*, which crystallises in colourless, lustrous leaflets, and melts at 182—184°; this is insoluble in alkalis, and dissolves in concentrated sulphuric acid with development of a yellow coloration.

Usnic acid has been isolated from *Hœmatomma coccineum* and *H. ventosum*, whilst the lichens *Stereocaulon coralloïdes*, *S. incrustatum*, *S. vesuvianum*, and *S. denudatum* contain psoromic acid.

*Placodin* is a copper-red substance obtained from *Placodium melanaspis* (Ach. and Fries), identical with *P. inflatum* (Körber); it crystallises from absolute alcohol in thin, pleochroïc plates, and melts and decomposes at 245°. It dissolves with difficulty in ether and chloroform, and is nearly insoluble in benzene; the solution in caustic soda is violet-brown, and concentrated nitric acid dissolves it with development of a yellow coloration.

*Stereocaulic acid* is isolated from *Stereocaulon alpinum* and *Lepra chlorina*, and crystallises from alcohol in white needles melting at 200—201°; it dissolves with difficulty in alcohol, ether, benzene, and chloroform, and carbonic anhydride does not precipitate the acid from its solution in sodium carbonate, which is yellow. The alcoholic solution develops a violet coloration with ferric chloride.

M. O. F.

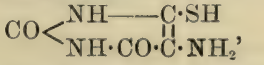
**Nitro-derivatives of Pyridine.** By Hugo Weidel and Ernst Murmann (*Monatsh.*, 1895, **16**, 749—759).—The authors obtain pyridine-$\beta$-sulphonic acid, in the exceptionally high yield of from 45 to 65 per cent., by the sulphonation of pyridine in presence of anhydrous aluminium sulphate with 33 per cent. anhydro-sulphuric acid at 330—350°. The sulphonic acid is first converted into $\beta$-hydroxypyridine (m. p. 129°), nd asubsequently into its acetyl derivative, and the latter is nitrated by the addition of nitric acid to an ice-cold solution in acetic anhydride; the action is then completed at the ordinary temperature, the acetic anhydride removed by distillation under diminished pressure, and the residue hydrolysed with sodium hydroxide. On adding hydrochloric acid to the product, a precipitate is obtained which, on exhaustion with boiling water, leaves an insoluble *nitro-β-hydroxypyridine.* This crystallises from alcohol in dull, yellow needles, and melts and decomposes at 295—298° (uncorr.). The aqueous solution, on exhaustion with ether, yields a *dinitro-β-hydroxypyridine* which crystallises from the ethereal solution in dull, yellow needles, and melts at 133° (uncorr.). A second *nitro-β-hydroxypyridine* crystallises from the aqueous solution in pale, lemon-yellow plates, and melts at 210—211° (uncorr.). G. T. M.

**Direct Introduction of Hydroxyl-groups into Hydroxyquinolines.** By Julius Diamant (*Monatsh.*, 1895, **16**, 760—772).—When 1-hydroxyquinoline is heated at 380°, with 10 times its weight of caustic soda and a little water, hydrogen escapes, and 1 : 2′-*dihydroxyquinoline*, $C_9H_7NO_2$, is formed; this crystallises from water in scales, melts with partial decomposition and sublimation at a temperature above 260°, and gives a dirty green coloration with ferric chloride. The *hydrochloride*, $C_9H_7NO_2,HCl + H_2O$, crystallises in yellowish-white needles or scales, and is very unstable. The *acetyl derivative*, $C_9H_6NO_2Ac$, forms crystalline scales, and melts at 244—247°. On oxidation with potassium permanganate in alkaline solution, the dihydroxyquinoline yields 6-hydroxyquinolinic acid, thus showing that the second hydroxyl-group is in the 2′ position.

Trihydroxyquinoline, $C_9H_7NO_3[(OH)_3 = 1 : 2' : ?]$, obtained on further heating the above-described dihydroxyquinoline with excess of caustic soda at 380°, crystallises in long, colourless needles; it is almost insoluble in ordinary solvents, but dissolves in borax solution and in alkalis, has an intensely sweet taste, and gives with ferric chloride a dirty green solution, which is turned brown by sodium carbonate. Trihydroxyquinoline may also be obtained by long-continued heating of hydroxyquinoline with excess of potash.

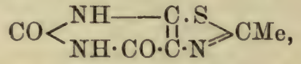
G. T. M.

**Formation of Thiazole Derivatives from Uric acid.** By Hugo Weidel and Ladislaus Niemilowicz (*Monatsh.*, 1895, **16**, 721—748).—When uric acid (2·5 grams) and ammonium hydrosulphide (15 c.c. of a solution obtained by adding 1 vol. of commercial ammonia to 2 vols. previously saturated with hydrogen sulphide) are heated together for four hours at 185°, 3-*amidouracyl 2-hydrosulphide*,

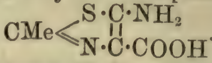
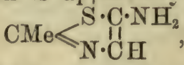


$$\mathrm{CO}<\begin{array}{l}\mathrm{NH{-}{-}C{\cdot}SH}\\ \qquad\quad\;\;\Vert\\ \mathrm{NH{\cdot}CO{\cdot}C{\cdot}NH_2}\end{array},$$

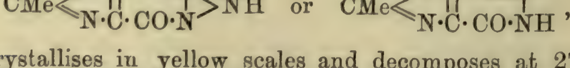
is formed. It crystallises from dilute acetic acid and from strong hydrochloric acid in slender needles, which do not melt at 300°, forms an unstable anhydrous *ammonia compound* having the composition $C_4H_5N_3SO_2,NH_3$, and on the addition of bromine yields uranil, isobarbituric acid, and other substances. On heating with a large excess of acetic anhydride, amidouracyl hydrosulphide yields the crystalline *acetyl* derivative, $C_8H_7N_3SO_3$, which is soluble in water, amylic alcohol and acetic acid, with partial decomposition, and melts and decomposes at a temperature above 300°. On treatment with water, or better, with a dilute alkaline solution, the acetyl compound yields the *ureide* of *μ-methyl-β-oxythiazole-α-carboxylic acid*,



$$CO<\begin{matrix}NH\text{——}C.S\\ NH\cdot CO\cdot \overset{\|}{C}\cdot N\end{matrix}>CMe,$$

which crystallises in felted masses of small needles, is soluble in water containing acids and alkalis, dissolves sparingly in alcohol and ethylic acetate, and gives the following salts. An *ammonium salt*, $C_6H_5N_3SO_2,NH_4\cdot OH$, crystallising in hair-like needles; a *sodium salt*, with $2H_2O$, crystallising in colourless needles; a *barium salt*, and an anhydrous crystalline *silver salt*, $C_6H_6N_3SO_2Ag$. When the ureide or its acetyl derivative is boiled with acetic anhydride and sodium acetate until no more carbonic anhydride escapes, and the excess of acetic anhydride is distilled off, the residue contains *β-acetylamido-μ-methylthiazole-α-carboxylonitrile.* This is insoluble in cold chloroform, but dissolves in the boiling solvent, from which it crystallises on cooling in long needles, and, when quickly heated, melts at 280—285°, undergoing partial sublimation. The residue also occasionally contains the *β-acetylamido-μ-methylthiazole-α-carboxylacetylamide*, which dissolves in cold chloroform and in water, melts at 176—178° (uncorr.), and, on further treatment with acetic acid and sodium acetate, gives the nitrile $C_7H_7N_3SO$. Each of these products from the residue is converted by dilute hydrochloric acid into *β-amido-μ-methylthiazole-α-carboxylamide*, $C_5H_7N_3SO + 2H_2O$, which crystallises in yellowish-white, monoclinic plates, [$a : b : c = 2{\cdot}783 : 1 : 1{\cdot}278$], is only sparingly soluble in cold water, melts with decomposition at a temperature above 300°, and, on fusion with potassium hydroxide at 260—280°, yields a crystalline mixture from which two substances were isolated, one soluble in alcohol and the other insoluble. The insoluble substance, formed only in small quantity, is *β-amido-μ-methylthiazole-α-carboxylic acid*,  $CMe<\begin{matrix}S\cdot \overset{}{C}\cdot NH_2\\ N\cdot \overset{\|}{C}\cdot COOH\end{matrix}$. It crystallises from water, in which it is fairly soluble, in scales, and decomposes at 200°. The soluble portion is apparently the *hydrochloride* of β-amido-μ-methylthiazole,  $CMe<\begin{matrix}S\cdot C\cdot NH_2\\ N\cdot \overset{\|}{C}H\end{matrix}$, which is readily dissolved by water, the solution giving an intense cherry-red coloration with ferric chloride, crystallises in scales, and decomposes at 250°.

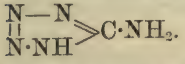
*Azimido-μ-methylthiazole-α-carboxylic acid*,



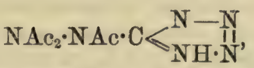
$$CMe<\begin{matrix}S\cdot C\text{——}N\\ N\cdot \overset{\|}{C}\cdot CO\cdot \overset{|}{N}\end{matrix}>NH \quad \text{or} \quad CMe<\begin{matrix}S\cdot C\cdot N{=}N\\ N\cdot \overset{\|}{C}\cdot CO\cdot \overset{|}{N}H\end{matrix},$$

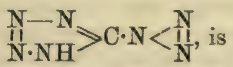
which crystallises in yellow scales and decomposes at 270—280°, is obtained on dissolving β-amidomethylthiazolecarboxylamide in hydrochloric acid, adding the requisite quantity of potassium nitrite, boiling the solution, evaporating in a vacuum, and finally extracting with alcohol.

G. T. M.

**Tetrazole Derivatives.** By JOHANNES THIELE and HARRY INGLE (*Annalen*, 1895, **287**, 233—265; compare Abstr., 1892, 1295, and 1893, i, 440).—*Amidotetrazole* is the name by which the authors now refer to amidotetrazotic acid (*loc. cit.*), which has the constitution,  $\left.\begin{array}{l}N-N\\ \|\\ N\cdot NH\end{array}\right>C\cdot NH_2$. The *cyanate* is obtained by adding potassium cyanate to an aqueous solution of the hydrochloride; it melts above 250°, and dissolves in dilute hydrochloric acid with liberation of carbonic anhydride, having the odour of cyanic acid. Boiling water decomposes the cyanate, giving rise to carbonic anhydride, ammonia, and amidotetrazole; an alcoholic solution of aniline yields phenylcarbamide. *Benzoylamidotetrazole* dissolves readily in alkalis, and melts and decomposes above 250°; the *acetyl* derivative crystallises in white leaflets melting at 269°, and has a strongly acidic reaction. Fuming hydrochloric acid does not attack amidotetrazole at 160—170°, but at 200—210° carbonic anhydride, ammonia, nitrogen, and hydrazine are formed, the last-named being produced in theoretical quantity.

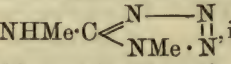
In preparing benzylidenetetrazylhydrazine (*loc. cit.*), an improved yield is obtained by regulating the quantity of hydrochloric acid in such a manner that at the conclusion of the operation excess of this agent is a minimum.

*Triacetyltetrazylhydrazine*,  $NAc_2\cdot NAc\cdot C\left<\begin{array}{r}N-N\\ \|\\ NH\cdot N\end{array}\right.$, crystallises from glacial acetic acid, and sinters at 140—150°, melting at 192°; it is strongly acidic, and does not develop a red coloration with ferric chloride. *Acetophenonetetrazylhydrazone* is obtained from aqueous tetrazylhydrazine hydrochloride and alcoholic acetophenone; it melts at 235°, and dissolves readily in alkali carbonates. *Acetonetetrazylhydrazone* is prepared from tetrazylhydrazine hydrochloride and acetone in presence of sodium acetate; it crystallises from water, and melts at 181·5°. *Tetrazylsemicarbazide* is formed on mixing warm, aqueous solutions of potassium cyanate and tetrazylhydrazine hydrochloride; it melts at 211° if slowly heated, at 218° when the temperature rises rapidly. The semicarbazide is acidic and strongly reducing, and is sparingly soluble in cold water; an alkaline solution of potassium permanganate oxidises it to tetrazolazocarboxylic acid, of which the *sodium* derivative was precipitated, ammonia being liberated at the same time.

*Tetrazylazoimide* (*diazotetrazoleimide*),  $\left.\begin{array}{l}N-N\\ \|\\ N\cdot NH\end{array}\right>C\cdot N\left<\begin{array}{r}N\\ \|\\ N\end{array}\right.$, is obtained by adding 5 c.c. of concentrated hydrochloric acid mixed with ice to an ice-cold solution of tetrazylhydrazine (2·3 grams) and sodium nitrite (2 grams); it crystallises from benzene in beautiful white needles. When rubbed slightly, or on heating gently, it explodes with greater violence than silver azoimide; it dissolves readily in water and acetone, but is insoluble in petroleum or ether, and yields azoimide when treated for several hours with boiling concentrated potash. The *silver* derivative is insoluble in cold, dilute, nitric acid, and explodes violently in the moist state; the *ammonium* derivative is a white powder, obtained on passing dry ammonia into a solution of tetrazylazoimide in benzene, and does not explode with greater violence than gunpowder. The ammonium salt is very soluble in water and methylic alcohol, but dissolves less readily in benzene. Fuming nitric acid decomposes tetrazylhydrazine at 170°, giving rise to hydrazine, carbonic anhydride, and nitrogen.

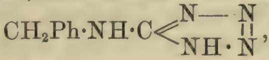
*Dihydrobenzylidenetetrazylhydrazine* is obtained by reducing benzylidenetetrazylhydrazine with sodium amalgam; it crystallises from alcohol, and melts and decomposes at 187—191°. The *sodium* derivative is colourless, and crystallises from dilute alcohol. The dihydro-derivative differs from benzylidenetetrazylhydrazine in dissolving in dilute mineral acids, and forming a *sulphate* which is sparingly soluble in cold water; it is, moreover, readily oxidised by mercuric oxide or an ammoniacal silver solution, whilst these agents attack benzylidenetetrazylhydrazine slowly when heated. When the dihydro-compound is treated with boiling hydrochloric or sulphuric acid, a small quantity of benzaldehyde is formed, but at 160° hydrochloric acid gives rise to benzylidene chloride and hydrazine. Acetonetetrazylhydrazone is indifferent towards sodium amalgam.

When sodium diazotetrazolate (*loc. cit.*) is reduced with alcohol, tetrazole is produced; this crystallises from ethylic acetate in aggregates of needles or leaflets, and melts at 156° (compare Bladin, Abstr., 1892, 1009). On heating tetrazole with hydrochloric acid for three hours at 200°, ammonium chloride is formed, but no hydrazine; it is completely decomposed by hot, concentrated sulphuric acid, yielding nitrogen and carbonic oxide. The *sodium* derivative of tetrazole contains $1H_2O$, and crystallises in thin prisms, which dissolve very readily in water. The *barium* derivative contains $3\frac{1}{2}H_2O$, and crystallises in large, transparent prisms, which become nearly anhydrous in the exsiccator; it belongs to the rhombic system, and has $a : b : c = 0{\cdot}5689 : 1 : 0{\cdot}7217$. The conductivity constants of tetrazole, of the sodium derivative, and of amidotetrazole have been determined.

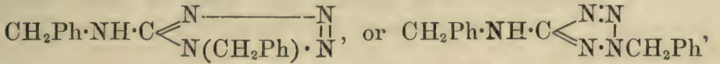
*Methylamidomethyltetrazole*,  $\mathrm{NHMe{\cdot}C}\begin{cases}\mathrm{N{-}{-}N} \\ \mathrm{NMe\cdot N}\end{cases}$, is obtained by heating anhydrous amidotetrazole (10 grams) with methylic iodide for three hours at 160—165°; it crystallises from ethylic acetate in leaflets, and begins to decompose at 80°. The substance is very hygroscopic, and its solution is strongly alkaline. The *hydrochloride* crystallises from alcohol in white needles, and melts and decomposes at 241°; the *picrate* melts and decomposes at 203°. The *aurochloride* crystallises from water in large plates, and melts at 164°; the *platinochloride* crystallises from alcohol in golden-yellow needles, and from water in large prisms, melting at 200°. The *nitrosamine* forms yellow needles, and yields nitrous acid under the influence of dilute mineral acids, nitrogen being evolved on treating it with potash.

*Methylamidotetrazole* crystallises from water in white needles, and melts at 218—220°; the aqueous solution is neutral. *Ethylamido-*

*ethyltetrazole hydrochloride* is very soluble in water and alcohol, and forms white needles melting at 232—233°.

*α-Benzylamidotetrazole* is obtained by boiling benzylic chloride (2 mols.) with amidotetrazole (2 mols.), sodium carbonate (1 mol.), water, and alcohol, until the odour of benzylic chloride is no longer perceptible; it melts at 191—192°, and is neutral. *β-Benzylamidotetrazole*,  $\mathrm{CH_2Ph{\cdot}NH{\cdot}C}\Big\langle\begin{array}{l}\mathrm{N—N}\\ \mathrm{NH{\cdot}N}\end{array}$, is formed on heating amidotetrazole (10 grams) with benzylic chloride (40 grams), caustic potash (50 grams), and dilute alcohol, for six hours; it melts at 181°, and dissolves in alkalis.

*Benzylamidobenzyltetrazole*,



$$\mathrm{CH_2Ph{\cdot}NH{\cdot}C}\Big\langle\begin{array}{l}\mathrm{N———N}\\ \mathrm{N(CH_2Ph){\cdot}N}\end{array}, \text{ or } \mathrm{CH_2Ph{\cdot}NH{\cdot}C}\Big\langle\begin{array}{l}\mathrm{N{:}N}\\ \mathrm{N{\cdot}NCH_2Ph}\end{array},$$

arises from the action of boiling benzylic chloride on anhydrous amidotetrazole, and is also obtained as a bye-product in the preparation of α-benzylamidotetrazole; it separates from alcohol and ether in lustrous crystals, and melts at 88·5°. The substance has an alkaline reaction. The *hydrochloride* crystallises in needles, and melts at 208—209°, and the *nitrate* at 122°; the latter salt and the *sulphate*, which melts at 173°, are sparingly soluble, and the *nitrite* crystallises from ether and melts at 108°. The *nitrosamine* crystallises in yellow needles melting at 105°, and when treated with boiling water yields *benzyloxybenzyltetrazole*, which crystallises from alcohol in small needles, and melts at 106°.

*β-Amidodibenzyltetrazole* is most conveniently prepared by heating amidotetrazole (5 grams), with caustic potash (15 grams), benzylic chloride (30 grams), and dilute alcohol in a reflux apparatus for two hours, adding a further quantity of caustic potash (10 grams), and again heating for two hours, or until the odour of benzylic chloride is no longer perceptible; it is also formed in the preparation of α- and β-benzylamidotetrazole. It crystallises from alcohol in lustrous needles, and melts at 169—170°; it is a neutral substance, and when oxidised in acid solution with potassium permanganate yields benzaldehyde. The *nitrosamine* crystallises from alcohol in lustrous, yellow plates, and melts at 97—98°.

*Benzylbenzylidenebenzyltetrazylhydrazine*,

$$\mathrm{CHPh{:}N{\cdot}N(CH_2Ph){\cdot}CN_4{\cdot}CH_2Ph},$$

is obtained by reducing the nitrosamine of benzylamidobenzyltetrazole in alcoholic solution with zinc dust and glacial acetic acid, and treating the base with alcoholic benzaldehyde; it is also formed when benzylidenetetrazylhydrazine is treated with boiling benzylic chloride. The substance is insoluble in water, and melts at 98°. *Benzylidene-β-dibenzyltetrazylhydrazine*, $\mathrm{CHPh{:}N{\cdot}N{\cdot}CN_4(CH_2Ph)_2}$, is obtained by heating a solution of benzylidenetetrazylhydrazine in caustic soda with benzylic chloride for several hours; it crystallises from alcohol in lustrous leaflets, and melts at 132—133°, yielding benzaldehyde when treated with boiling dilute sulphuric acid.

*α-Benzylidenebenzyltetrazylhydrazine* crystallises from alcohol, and melts at 161°; the *hydrochloride*, which melts at 246°, is obtained as a bye-product in preparing benzylbenzylidenebenzyltetrazylhydrazine. *α-Benzyltetrazylhydrazine* is obtained by eliminating benzaldehyde from the benzylidene derivative by means of boiling hydrochloric acid; it crystallises from water in lustrous leaflets, and melts at 123°. The aqueous solution has a strongly reducing action, and yields the benzylidene derivative when treated with benzaldehyde. The *hydrochloride* crystallises in long needles, and melts and decomposes at 200°.

*β-Benzylidenebenzyltetrazylhydrazine* is prepared by heating benzylidenetetrazylhydrazine (2 grams) with sodium carbonate (1 gram), benzylic chloride (1·3 gram), and a small quantity of water and alcohol; it crystallises from alcohol and melts at 199°. Boiling mineral acids resolve the substance into benzaldehyde and β-benzyltetrazylhydrazine.

*α-Tribenzyltetrazylhydrazine* is a bye-product in the formation of benzylidene-β-dibenzyltetrazylhydrazine, and also arises from treatment of tetrazylhydrazine in alkaline solution with benzylic chloride; it crystallises from ethylic acetate in white needles melting at 153°, and is indifferent towards boiling dilute sulphuric acid.

*β-Tribenzyltetrazylhydrazine* is obtained by heating benzylidenetetrazylhydrazine (2 grams) with benzylic chloride (5 grams) and a 25 per cent. solution of caustic soda (10 c.c.), benzaldehyde being eliminated. It melts at 121°, and is insoluble in acids and alkalis, undergoing no change when heated with these agents. M. O. F.

**Effect of Light on Diastase.** By JOSEPH R. GREEN (*Ann. Agron.*, 1895, **21**, 442—443; from *Annals of Bot.*, 1894, **8**, 370).—Sunlight and electric light destroy diastase, the violet rays of the spectrum having the greatest effect, whilst on the other hand, the less refrangible rays have a slightly favourable effect; the colouring matter of the covering of barley thus protects the diastase from injury by light. Diastase which has been exposed to light, and afterwards kept in darkness, gradually loses its power, the destructive action induced by light continuing.

N. H. J. M.

**Maltase and the Alcoholic Fermentation of Maltose.** By ÉMILE BOURQUELOT (*J. Pharm.*, 1895, [6], **2**, 97—105).—The question whether the enzyme, by which maltose is hydrolysed into glucose, is a chemical individual distinct from the known enzymes, such as diastase and invertase, has not yet been decided. It certainly has not been obtained in a state of purity, for the various preparations that have been made, although possessing the common property of hydrolysing maltose, differ in their powers of hydrolysing other carbohydrates; but it is hardly likely, as E. Fischer seems to suppose, that there are many maltohydrolytic enzymes differing in their powers of hydrolysing other carbohydrates, for all the well-known enzymes of this class are characterised by the limitation of their powers to the hydrolysis of single carbohydrates.

It is now fully established that there is a maltohydrolytic enzyme in the pancreas and small intestine of various animals, but the question of the presence of such an enzyme in plants has not hitherto been investigated.

The author finds that when the common moulds, *Aspergillus niger* and *Penicillium glaucum*, are cultivated in an aqueous medium containing maltose, with tartaric acid and the usual salts, a considerable amount of the maltose is hydrolysed into glucose; and by grinding the moulds with sand, and extracting them with water, liquids can be obtained, from which a maltohydrolytic enzyme is precipitated by alcohol.

The lactic fermentation of maltose, like the alcoholic fermentation, is preceded by its hydrolysis; Fischer's isolation of glucosazone in the latter case is conclusive, and the author has proved the presence of glucose indirectly in the former case. When chloroform is added to a solution of maltose, or of a mixture of maltose and levulose, in alcoholic fermentation, the reducing power of the liquid continues to increase, whilst the rotatory power diminishes, and this can only be due to the continued formation of glucose by the hydrolytic action of an enzyme, during the suspension of the activity of the yeast.

With regard to the presence of a similar enzyme in blood, Dubourg (*Inaug. Diss.*, Paris, 1889) has proved that the blood of rabbits kept on an amylaceous diet has the power of hydrolysing maltose. It is thus clear that the assimilation of maltose in animals is always preceded by its hydrolysis into glucose.

The author inclines to the opinion that the maltohydrolytic enzyme, maltase, is a chemical individual distinct from the other well-known enzymes. JN. W.

**Preparation of Crystalline Bile acids and their Relationship to Colouring Matters.** By RICHTER (*Chem. Centr.*, 1895, i, 282—283; from *Deut. Med. Woch.*, 1894, **21**; *Vereinsbeilage*, i, 2—3). —Ox bile (250 c.c.) is treated with concentrated ferric chloride solution (10—15 c.c.), and the precipitate dissolved in sulphuric acid (60 per cent.); the residue consists chiefly of glycocholic acid; the solution, which contains the taurocholic acid, is freed from iron by means of ammonia, the filtrate diluted, sulphuric acid (10 per cent.) added until a precipitate is formed, and then shaken with ether, after 24 hours, crystals of practically pure glycocholic (? taurocholic) acid are deposited. The two acids may be separated by dissolving them in soda, and acidifying with sulphuric acid; glycocholic acid is first precipitated, and the taurocholic acid is then deposited as an oil which crystallises after some time. When these acids are treated by Hoppe-Seyler's method with ammonia and concentrated sulphuric acid, and the fluorescent product exposed to air, shaken with chloroform, and water added, a violet colour is produced; this, on further dilution, becomes deep blue, and then changes spontaneously to green. The colours are stable in the dark, but are affected by light, and their spectra resemble those of bile pigments. Human bile, and that of an ox suffering from jaundice, gave similar results, but the glycocholic acid appears to be absent. J. B. T.

**Constitution of Vegetable Proteïds.** By ÉMILE C. A. FLEURENT (*Compt. rend.*, 1895, **121**, 216—219).—Vegetable proteïds can be divided into two groups, namely, those, such as gluten, caseïn, and vegetable fibrin, in which the ratio of ammoniacal nitrogen estimated to that calculated is greater than unity, and those, such as legumin and vegetable albumin, in which the ratio is less than unity. The fixed residue from gluten, after boiling with barium hydroxide solution (Abstr., 1894, i, 214), consists mainly of tryrosine, the caproic leucine, and the leucine, $C_4H_7NO_2$, whilst the fixed residue from legumin is a mixture of tryrosine, alanine, butalanine, and the different glucoproteïns. In both animal and vegetable proteïds, the water necessary for hydrolysis combines partly with special groups yielding ammonia, and carbonic, oxalic, and acetic acids, and partly with a special nucleus, yielding a fixed residue. The formula of the fixed residue from vegetable proteïds, expressed in the simplest general terms, is $C_nH_{2n}N_2O_5$, whilst that from animal proteïds is $C_nH_{2n}N_2O_4$. The nucleus of all the vegetable proteïds examined can be represented by the general formula $C_nH_{2n-4}N_2O_3$, whilst Schützenberger found for the nucleus of egg albumin and its congeners the formula $C_nH_{2n-4}N_2O_2$. There is therefore a difference of an atom of oxygen. In both cases, as many molecules of water are necessary to hydrolysis as there are atoms of nitrogen present; in both cases also, hydrolysis takes place in two stages, and it follows that the nucleus of vegetable proteïds is a mixture of imido-compounds, which are converted by hydrolysis into amido-acids. Gluten, caseïn, and vegetable fibrin contain a glutamine group, whilst legumin and vegetable albumin contain an asparagine group (Abstr., 1894, i, 571), and to these respectively is due the departure from unity of the ratios between the found and calculated quantities of ammoniacal nitrogen. The glutamine and asparagine groups do not exist in animal proteïds, and Schützenberger has found that the quantities of ammoniacal nitrogen found and calculated are identical. These groups are the first to undergo hydrolysis, and give rise to the ammonia which is obtained by boiling gluten or legumin with alkali solutions under ordinary pressure. C. H. B.

**Albumoses.** By Hugo Schrötter (*Monatsh.*, 1895, **16**, 609—618; compare Abstr., 1894, i, 215).—The method of distinguishing albumoses and peptones proposed by Kühne is valueless, since these substances and their respective salts all give precipitates with an aqueous solution of ammonium sulphate. Albumoses, however, are perfectly differentiated from peptones by their large percentage of nitrogen, by their high molecular weight, and by the still more important fact that they contain sulphur, whilst peptones contain none. The generally accepted view, that by the action of ferments or acids, albumin is first of all converted into albumoses, and finally into true peptones, is incorrect. As a matter of fact, when albumin is heated with an acid, a direct conversion into peptones, without the formation of albumoses, takes place, and this is confirmed by the fact that albumoses, when treated with an acid, are in a great measure decomposed, and give rise to no peptones. G. T. M.

# Organic Chemistry.

**Action of Heat on Ethylene.** By VIVIAN B. LEWES (*Proc. Roy. Soc.*, 1895, **57**, 394—404).—The apparatus and methods of analysis were the same as described in the previous paper (Abstr., 1894, i, 481), except that a platinum tube was used as the decomposing chamber, and a gas combustion furnace as the source of heat. The experiments show: (1) That the initial decomposition of ethylene by heat is very rapid, but that this primary decomposition is only very slowly completed, owing to secondary reactions, which tend to re-form ethylene. Thus when only 1 in. of the platinum tube was heated, 80 per cent. of the ethylene was decomposed, and with 18 in. heated only 93·7 per cent. (2) That increase in the rate of flow of the gas through the platinum tube diminishes the decomposition when the heated area is small, but has very little effect when the heated surface is large. (3) That dilution has but little effect on the decomposition; and (4) that the decomposition of ethylene is mainly due to radiant heat. J. J. S.

**Combination of Mercuric Cyanide with Bromides and with Iodides.** By RAOUL VARET (*Compt. rend.*, 1895, **121**, 398—400, and 499—501; compare this vol., ii, 88 and 148).

**Double Decompositions between Mercuric Cyanide and Salts of Alkali and Alkaline Earth Metals.** By RAOUL VARET (*Compt. rend.*, 1895, **121**, 501—502).—Fluorides, chlorides, sulphates, nitrates, carbonates, acetates, and picrates of the metals of the alkalis or alkaline earths do not interact with mercuric cyanide. Bromides behave similarly, but there is a slight exchange of acids and bases. Iodides, on the other hand, interact, and the change is limited by the formation of salts of the type $Hg(CN)_2,M''(CN)_2,HgI_2$. With the sulphides there is complete double decomposition. There is more or less complete decomposition when the acid in combination with the other salt displaces (when in the free state) hydrocyanic acid from the mercuric salt; if this is not the case, there is no appreciable interaction. C. H. B.

**Calcium Cyanate, a Nitrogenous Manure.** By CAMILLE FAURE (*Compt. rend.*, 1895, **121**, 463).—Calcium cyanate can be prepared in large quantities in the electrical furnace, limestone and carbon being first heated at 1500°, then at 2500°, in presence of excess of nitrogen, and finally at 2500° in a current of air. C. H. B.

**Alcoholates.** By HENRI LESCOEUR (*Compt. rend.*, 1895, **121**, 691—692).—Solutions of sodium ethoxide in ethylic alcohol, and the products obtained by evaporation, have the following vapour pressures at 60°. Saturated solution, 138 mm.; product nearly dry, 135 mm.; product EtNaO + 1·7 EtOH, 60 mm.; product EtNaO + 0·8 EtOH, 56 mm.; effloresced product, 54 mm.; almost pure EtNaO, less than 18 mm.

A compound EtNaO + 2EtOH is therefore well defined by its vapour pressure at 60°. The vapour pressure varies as follows; at 40°, 14 mm.; at 60°, 57 mm.; at 80°, 172 mm. In a dry atmosphere at the ordinary temperature, sodium ethoxide alcoholate effloresces, and yields sodium ethoxide.

Similar observations on solutions of sodium hydroxide in alcohol gave the following results at 100°. Fused product, NaOH + 3EtOH, more than 300 mm.; product partially solidified, more than 300 mm.; solid product, NaOH,EtOH, 215 mm.; effloresced product, 207 mm.; ditto, 200 mm.; almost pure NaOH, less than 30 mm. A compound NaOH + EtOH is therefore defined; its vapour pressure is 35 mm. at 76°; 207 mm. at 100°; 275 mm. at 105°. When sodium hydroxide is dissolved in boiling alcohol, and the solution is cooled, it deposits small scales, which seem to have the composition NaOH + 3EtOH; they alter very rapidly in moist air, melt easily, and give off alcohol when heated. These compounds are true alcoholates of sodium hydroxide.
C. H. B.

**Action of Chlorine on Normal Propylic Alcohol.** By André Brochet (*Compt. rend.*, 1895, **121**, 648—650).—The action of chlorine on normal propylic alcohol in the cold results in phenomena similar to those observed with methylic and isobutylic alcohols. In the end the liquid separates into an upper layer consisting of water, hydrochloric acid, unaltered alcohol, and chloropropaldehyde, and a lower layer consisting of unsymmetrical *dichloropropylic ether*,

$$CHMeCl{\cdot}CHCl{\cdot}O{\cdot}CH_2{\cdot}CH_2Me,$$

a colourless, very mobile liquid, with a characteristic and very persistent odour. It boils at 80° under a pressure of 15 mm., and at 176° under 762 mm.; sp. gr. at 15°/4° = 1·129; refractive index $n_D = 1{\cdot}447$ at 16°. When boiled with water, the dichloropropylic ether yields a mixture of α-chloropropaldehyde and chlorodipropylic propional, $CMeCl_2{\cdot}CH(OPr)_2$.

*α-Chloropropaldehyde*, after being dried by treatment with an equal volume of sulphuric acid at −20°, is a colourless, very mobile liquid, which boils at 86° under a pressure of 755 mm.; sp. gr. at 15°/4° = 1·182°; refractive index $n_D = 1{\cdot}431$ at 17°. It does not yield crystals of a polymeride in contact with sulphuric or hydrochloric acid, but there is some evidence that it very slowly polymerises in contact with a small quantity of hydrochloric acid. When oxidised with potassium permanganate, with addition of alkali, it yields acetic, carbonic, and hydrochloric acids.

*Chlorodipropylic propional* is obtained by the action of water or propylic alcohol on dichloropropylic ether. It is a colourless, mobile liquid, which boils at 203° under a pressure of 755 mm., and, like all acetals, is very stable; sp. gr. at 15°/4° = 0·990; refractive index $n_D = 1{\cdot}430$ at 16°.
C. H. B.

**Trimethylenic Glycol as a Bye-product in the Glycerol Manufacture.** By Arthur A. Noyes and Willard H. Watkins (*J. Amer.*

*Chem. Soc.*, 1895, **17**, 890—891).—The authors have succeeded in isolating trimethylenic glycol from a specimen of glycerol of low specific gravity. This was probably formed, before saponification, by the fermentation of the glycerol present in the fat. The presence of this glycol in glycerol used for nitroglycerol manufacture might be a source of danger, owing to its violent reaction with nitric acid.

J. J. S.

**Pentaglycol: a Dihydric Alcohol synthesised from Formaldehyde and Isobutaldehyde.** By M. Apel and Bernhard Tollens (*Annalen*, 1895, **289**, 36—46; compare Abstr., 1894, i, 353).—*Pentaglycol iodhydrin*, $CH_2I{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$, is obtained by heating pentaglycol with hydriodic acid and phosphorus for two hours; it is a pale yellow oil, which boils at 60° in a vacuum. *Methylenepentaglycol*, $C_5H_{10}{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}CH_2$, boils at 126°.

M. O. F.

**Boiling Point of Nitroglycerol.** By Cornelius A. Lobry de Bruyn (*Rec. Trav. Chim.*, 1895, **14**, 131—133).—The author refers to the value obtained by Champion (*Compt. rend.*, 1871, **73**, 42) for the boiling point of nitroglycerol, and criticises the method adopted by this chemist.

A small quantity of nitroglycerol, contained in a boiling flask, was heated in a bath of glycerol to 160°, under a pressure of 15 mm., the pressure being diminished by means of a water pump. No nitroglycerol distilled over under these conditions, but the substance commenced to volatilise. The author believes that if a mercury pump had been employed, the nitroglycerol would have distilled. This negative result renders it certain that the boiling point of nitroglycerol at the ordinary temperature cannot be 185°, as stated by Champion.

Champion and Lorm have published values for the vapour pressure of nitroglycerol, according to which the boiling point of the compound would be below 200°; these are likewise not in accord with the author's experience.

A. R. L.

**Compounds of Formaldehyde with Polyhydric Alcohols.** By M. Schulz and Bernhard Tollens (*Annalen*, 1895, **289**, 20—34; compare Abstr., 1894, i, 438).—The compounds dealt with in this paper have been already described by the authors (*loc. cit.*), the class name formal being used instead of formacetal.

M. O. F.

**Penta-erithrytoldibenzal.** By M. Apel and Bernhard Tollens (*Annalen*, 1895, **289**, 34—35; compare Abstr., 1894, i, 353).—*Dibenzylidenepenta-erithrytol*, $C_5H_8O_4(C_7H_6)_2$, melts at 160°.

M. O. F.

**Anhydro-enneaheptitol from Formaldehyde and Acetone.** By M. Apel and Bernhard Tollens (*Annalen*, 1895, **289**, 46—51; compare Abstr., 1894, i, 353).—The authors have already described *anhydro-enneaheptitol*, $OH{\cdot}CH(C[CH_2{\cdot}OH]_3)_2$ (*loc. cit.*), and a more detailed account of the properties of the substance is now supplied.

M. O. F.

**Action of Dilute Alkalis on the Carbohydrates.** By Cornelius A. Lobry de Bruyn (*Rec. Trav. Chim.*, 1895, **14**, 156—165).—When a 4 per cent. aqueous solution of ordinary glucose (500 c.c.) is treated with normal potassium hydroxide solution (10 c.c.), the optical activity diminishes, until at the end of 135 hours it has sunk approximately to zero, at which it remains constant. The solution is now found to require only about one-third the calculated quantity of acid to neutralise it; the neutral solution still remains optically inactive. The same result is obtained when glucose is treated at the ordinary temperature with a more concentrated solution of potassium hydroxide; the author separated ordinary glucose from the neutralised product. Other bases, notably ammonia and barium hydroxide, behave towards glucose in the same manner. Xylose and galactose likewise undergo a change in rotatory power when treated with dilute alkalis.

A. R. L.

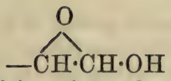
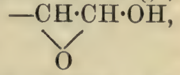
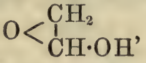
**Action of Alkalis on the Sugars. Reciprocal Transformation of Glucose, Fructose, and Mannose.** By Cornelius A. Lobry de Bruyn and W. Alberda van Ekenstein (*Rec. Trav. Chim.*, 1895, **14**, 201—216, and *Ber.*, 1895, **28**, 3078—3082).—The optically inactive syrup which is obtained by the action of potassium or sodium hydroxide, or ammonia on glucose, is also formed by the action of calcium hydroxide, sodium, or potassium carbonate, or magnesium oxide. When, however, the action is prolonged, calcium hydroxide leads to the formation of saccharinic acid, which is not the case with potassium or sodium hydroxide (compare Kiliani, *Ber.*, 1882, **15**, 2960). The speed with which the optical activity is attained is dependent on the temperature and concentration of the solution; the most favourable temperature being 70°. Glucose (100 grams) dissolved in water (400 c.c.) and treated at this temperature with calcium hydroxide (5 grams), is transformed in a few hours. The calcium is readily precipitated by passing a current of carbonic anhydride through the solution. By this transformation, glucose is, in part, converted into mannose, which was isolated and estimated by means of its insoluble phenylhydrazone, and, in part, into fructose; a certain portion of the glucose remains unaltered, whilst another portion is converted into acids.

Fructose is also partially converted into glucose and mannose on being similarly treated with alkalis or alkaline earths, whilst mannose is, in like manner, partially converted into glucose and fructose. The authors' results are drawn up in the form of a table.

This reciprocal transformation is conditioned by a state of equilibrium which may be represented by the symbol

$$\text{Glucose} \leftrightarrow \text{fructose} \leftrightarrow \text{mannose}.$$

Actual equilibrium is never established, however, because simultaneous decomposition into acids occurs. Galactose is not formed in this reaction.

As an explanation of the mechanism of the changes which occur during this transformation, it is suggested that the two end groups in the molecule of glucose, —CH(OH)·CHO, first combine with a molecule of water, which is subsequently split off in such a manner that the complex  $—\overset{O}{\widehat{CH\cdot CH}}\cdot OH$ results, which then passes, by intramolecular transposition, into the complex $—CO\cdot CH_2\cdot OH$, which exists in the ordinarily accepted formula for fructose. By an inverse change, fructose may be assumed to give rise to the complex  $—\underset{O}{\underbrace{CH\cdot CH}}\cdot OH$, stereoisomeric with that above mentioned, which, by addition and loss of water, would give mannose; or the two end groups in the molecule of fructose, by addition and loss of water, may be assumed to be converted into the complex  $O<\begin{matrix}CH_2\\ |\\ CH\cdot OH\end{matrix}$, which, by intramolecular transposition, may give rise to the complex $—CH(OH)\cdot CHO$.

The reciprocal transformation of the three sugars evidently plays a *rôle* in the chemical changes which occur in the tissues of plants. The reaction demonstrates the necessity of observing caution in drawing conclusions from experiments on the sugars made in alkaline solutions. Thus it was long thought that mannitol was the alcohol corresponding with glucose, because that alcohol is one of the products formed by reducing glucose with sodium amalgam; this was, however, disproved by E. Fischer.

The reaction also explains the fact that the technical invert sugar syrups, after the treatment with lime, are almost optically inactive, instead of being lævorotatory. An investigation of certain "foreign syrups" has shown that they contain notable quantities of mannose.

A. R. L.

**Sugars richer in Carbon from Galactose.** By EMIL FISCHER (*Annalen*, 1895, **288**, 139—157; compare Abstr., 1890, 597).—*α-Galaheptonic acid* is the galactosecarboxylic acid obtained by Maquenne and Kiliani. Galactose (100 grams) is dissolved in warm water (150 grams) and treated at 0° with hydrogen cyanide (28 c.c.), a few drops of aqueous ammonia being also added; after remaining at 0° during 24 hours, a quantity of the amide amounting to 25 per cent. of the material employed may be removed by filtration, a further separation taking place during two following days. The amide is dissolved in boiling aqueous barium hydroxide and heated until ammonia is no longer perceptible; the hot liquid is then exactly neutralised with sulphuric acid, boiled with animal charcoal, filtered and evaporated. The syrup is then heated for several days in a porcelain basin on the water bath with successive quantities of alcohol, and by this treatment yields the lactone (*loc. cit.*), which crystallises from methylic alcohol in long needles, melting at 151° (corr.) after softening at 142°; at 20° it has the specific rotatory power $[\alpha]_D = -52\cdot3°$. The *phenylhydrazide* dissolves in 25 parts of boiling water, and crystallises in colourless, lustrous needles; it becomes brown and evolves gas at 226° (corr.) when rapidly heated.

*α-Galaheptose* is prepared by reducing the lactone in ice-cold solution with sodium amalgam; it is obtained as a sweet, colourless syrup on decomposing the hydrazone with benzaldehyde. The sugar is extremely soluble in water, but dissolves with great difficulty in absolute alcohol; the aqueous solution is feebly lævorotatory, and is not fermented by yeast. The *phenylhydrazone* dissolves in 30 parts of boiling water, and crystallises in colourless needles; it evolves gas and melts at 205° (corr.). The *osazone* dissolves in 200 parts of boiling alcohol, and crystallises in yellow needles; it melts and decomposes at 224° (corr.).

*α-Galaheptitol* is obtained by reducing α-galaheptose with sodium amalgam in a solution neutralised with sulphuric acid; it crystallises in colourless needles and melts at 187—188° (corr.). The substance is very readily soluble in water and has a sweet taste, but dissolves with difficulty in absolute alcohol; in a concentrated solution of borax at 20°, it gave $[\alpha]_D = -4{\cdot}35°$.

*Gala-octonic acid* is obtained from α-galaheptose by means of hydrogen cyanide. On decomposing the amide with aqueous barium hydroxide, the *lactone* is formed, melting at 225—228° (corr.); at 20° it dissolves in 20 parts of water, but is scarcely soluble in absolute alcohol; the aqueous solution gives $[\alpha]_D = +64{\cdot}0°$ at 20°. The *phenylhydrazide* is colourless, and melts and decomposes at 235° (corr.); the *barium* salt is crystalline and anhydrous.

*Gala-octose* crystallises in colourless lustrous leaflets containing $1H_2O$, and melts at 109—111° (corr.); it is strongly lævorotatory. The *phenylhydrazone* crystallises in slender leaflets and melts at 205—210° (corr.); the *osazone* forms slender yellow needles insoluble in water, and melts at 226—231° (corr.).

*Gala-octitol* crystallises from 90 per cent. alcohol in slender needles, and from water in colourless, rectangular plates; it melts at 230—232° (corr.), does not reduce Fehling's solution, and is tasteless.

*β-Galaheptonic acid* is obtained from the brown mother-liquor containing the amide of the α-acid; the action of water and pyridine at 135—140° converts it into the α-modification. The *phenylhydrazide* dissolves in 4 parts of boiling water, and separates in colourless crystals melting at 185°; the aqueous solution at 20° gave $[\alpha]_D = -6{\cdot}32°$.

*β-Galaheptose* crystallises in prisms and melts and decomposes at 195—199° (corr.); 10 minutes after preparing an aqueous solution at 20° it gave $[\alpha]_D = -22{\cdot}5°$, the final reading after 24 hours being $[\alpha]_D = -54{\cdot}4°$ at the same temperature.

The dibasic acid obtained from α-galaheptonic acid has been described by Kiliani; at 20° the aqueous solution gave $[\alpha]_D = +15{\cdot}08°$. The *acid* obtained from β-galaheptonic acid by oxidation with nitric acid is a syrup; the *calcium* salt contains $2H_2O$, which is lost at 130°, and the solution in hydrochloric acid is dextrorotatory.

M. O. F.

**Ammonical Derivatives of Milk Sugar, Maltose, Galactose, Xylose, Arabinose, and Rhamnose.** By Cornelius A. Lobry de Bruyn and Frederik H. van Leent (*Rec. Trav. Chim.*, 1895, **14**, 134—149, and *Ber.*, 1895, **28**, 3082—3084; compare Abstr., 1894, i, 221; 1895, i, 7 and 640).—Dry gaseous ammonia has no action on ordinary hydrated milk sugar, or on its anhydride at the ordinary temperature. A concentrated solution in aqueous ammonia exhibits the normal rotation at first; the rotation diminishes, however, after some days, but the ultimate value cannot be determined on account of the darkening of the solution.

*Lactose ammonia*, $C_{12}H_{22}O_{11},NH_3$, an additive compound analogous to aldehyde ammonia, is obtained when ordinary hydrated milk sugar is dissolved in methyl alcoholic ammonia, and the solution concentrated after being kept for 11—18 days. It readily loses ammonia both in the dry state, and also when its aqueous solution is distilled; in the latter case about half the ammonia passes over, the remainder being retained by the coloured substances which are produced. Determinations of the molecular weight of lactose ammonia by the cryoscopic method indicate that the substance is partially dissociated in dilute solutions. The author failed to obtain salts of the compound.

*Maltosamine*, $C_{12}H_{21}O_{10}\cdot NH_2$, is best obtained by dissolving hydrated maltose in alcoholic ammonia; it melts and decomposes at 165°, and loses the whole of its ammonia when boiled with dilute sulphuric acid.

When galactose is dissolved in methylic alcoholic ammonia two compounds are formed:—*galactosamine ammonia*, $C_6H_{11}O_5\cdot NH_2,NH_3$, which melts at 113—114°, and *galactosamine*, $C_6H_{11}O_5\cdot NH_2$, which melts and decomposes at 141°; the crystals of the latter can be kept in an ordinary desiccator without losing ammonia. If either of the compounds is boiled with dilute sulphuric acid, an amount of acid is neutralised corresponding with the combined ammonia.

*Xylosamine*, $C_5H_9O_4\cdot NH_2$, melts and decomposes at about 130°.

*Arabinosamine*, $C_5H_9O_4\cdot NH_2$, melts at about 124°.

*Rhamnosamine methylic alcoholate*, $(C_6H_{11}O_4\cdot NH_2)_2,MeOH$, is obtained by dissolving rhamnose in methylic alcohol; it may be recrystallised from methylic alcohol, and melts at about 116°, but it commences to lose ammonia below this temperature. The *ethylic alcoholate* melts at 80° with the loss of alcohol and some ammonia.

The authors have as yet failed to obtain crystalline ammoniacal derivatives from mannose and glucoheptose. A. R. L.

**Action of Diastase on Isomaltose.** By CARL J. LINTNER (*Chem. Centr.*, 1895, i, 91; from *Zeit. ges. Brauw.*, 1894, **17**, 378; compare this vol., i, 4).—The author has previously stated that isomaltose is readily converted by diastase into maltose. Further observations have shown that the process is not complete; in one case only 30 per cent. was changed. Experiments seem to show that isomaltose, obtained by the action of oxalic acid on starch, is not acted on at all by diastase. The author thinks that this may probably be accounted for by assuming that there are two stereoisomeric isomaltoses.

J. J. S.

**Isomaltose.** By EMIL FISCHER (*Ber.*, 1895, **28**, 3024—3028; compare Abstr., 1891, 412, and Brown and Morris, Trans., 1895, 709).—Ost (*Chem. Zeit.*, 1895, No. 67) has stated that Fischer's synthetical isomaltose is merely impure maltose; in reply, the author states that his isomaltose is quite different from maltose, as it is not fermented by yeast, nor yet by the enzymes of yeast. Isomaltosazone is best recrystallised first from water, and, finally, several times from ethylic acetate; it cannot be obtained in the pure state by crystallisation from alcohol, the method employed by Ost. The melting point lies between 140° and 155°, according to its purity. Isomaltose, after treatment with yeast and after dialysis, yields an osazone, which melts at 158°, and has a specific rotatory power $[\alpha]_D = +7°$. The author has not succeeded in obtaining the pure carbohydrate.

J. J. S.

**Action of Heat on Starch dissolved in Glycerol.** By Karl Zulkowski and Boh. Franz (*Bied. Centr.*, 1895, **24**, 557—558; from *Ber. Oest. Ges. Förd. Chem. Ind.*, **16**, 120—127).—When pure potato starch is heated with glycerol at 190°, *soluble starch* is produced; this is precipitated by alcohol, and by lime and baryta. It changes back to ordinary starch when kept either in the dry state, or in concentrated aqueous solution. Soluble starch gives a splendid indigo coloration with iodine solution.

*Erythrodextrin* is formed when starch and glycerol are heated at 200° until the product gives a cherry colour with iodine; it is then precipitated with alcohol and washed with alcohol. It is a white, sandy powder, which is not hygroscopic, and is only precipitated from its aqueous solution by baryta after the addition of alcohol.

*Achroodextrin* is produced by heating the mixture at 210° until the product no longer gives a red colour with iodine; it is hygroscopic, and the solution is coloured distinctly brownish-yellow by extremely dilute iodine solution. When the heating at 210° is more prolonged, a product is obtained which is soluble in alcohol, but is precipitated on adding saturated baryta solution until strongly alkaline; the product consists of two substances, one a transparent, hygroscopic mass, very like gum arabic, soluble in strong alcohol, the other less transparent and hygroscopic, and soluble only in dilute alcohol.

Erythrodextrin and achroodextrin reduce distinctly, but feebly, whilst the products soluble in alcohol do not reduce at all. The rotatory power of the partially purified substances was found to be as follows:—Soluble starch, 188·3; erythrodextrin, 181·0; achroodextrin, 173·5; products soluble in dilute and in strong alcohol, 151·5 and 98·9 respectively.

N. H. J. M.

**Action of Oxalic acid on Inulin.** By Georg Düll (*Chem. Zeit.*, 1895, **19**, 166 and 216—217).—The object of this research was to find out whether the dextrin compounds (levulins) produced during the hydrolysis of inulin with dilute sulphuric acid are really intermediate products in the inversion of the inulin into levulose, or are secondary products of reversion. The molecular weight of pure inulin was found to be 2950, which agrees with the formula, $(C_6H_{10}O_5)_{18}$, or $(C_6H_{10}O_5)_{18} + H_2O$, and the rotatory power to be $[\alpha]_D = -40°$.

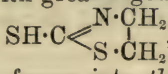
A table is given, showing the molecular weights and rotatory powers of varying mixtures of inulin and levulose.

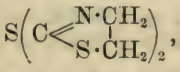
As the result of numerous experiments made with varying quantities of oxalic acid, the author concludes that no intermediate dextrin-like substances (levulins) are formed, so that, beyond doubt, the levulins produced by the action of dilute sulphuric acid on inulin are really reversion products of levulose.

Directions for preparing crystalline levulose by the action of oxalic acid on inulin are given.

It is further shown that if oxalic acid is allowed to act on levulose for some time under pressure, a substance, $C_6H_6O_3$, which is a derivative of furfuraldehyde, is obtained. Sorbose also gives the same product (compare Kiermayer, this vol., i, 144). J. J. S.

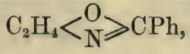
**Vinylamine.** By SIEGMUND GABRIEL and ROBERT STELZNER (*Ber.*, 1895, **28**, 2929—2938; compare Abstr., 1888, 668).—When bromethylamine hydrobromide, prepared by heating bromethylphthalimide with hydrogen bromide and acetic acid, is treated with 33 per cent. potash, and the resulting solution is distilled, a solution of vinylamine is obtained, from which the free base separates when solid potash is added. The base boils at 55—56°, fumes in the air, has a strongly ammoniacal smell, mixes with water, attacks the skin, and has a sp. gr. = 0·8321 at 24°. The *oxalate*, $C_2H_5N,C_2H_2O_4$, forms slender needles, is readily soluble in water, and melts and decomposes at 115°.

When an aqueous solution of vinylamine is heated for some hours at 100°, the base undergoes alteration, a syrupy mass being left after evaporation, from which crystalline salts cannot be obtained. Alcohol does not produce a similar change. *Iodethyltrimethylammonium iodide*, $CH_2I{\cdot}CH_2{\cdot}NMe_3I$, is formed by the action of methylic iodide on the base. The melting point of this substance, stated by Schmidt as 230—231°, varies with the rate at which the substance is heated. Vinylamine combines with great vigour with carbon bisulphide, thiazoline $\mu$-hydrosulphide,  $SH{\cdot}C<\begin{matrix}N{\cdot}CH_2\\ |\\ S{\cdot}CH_2\end{matrix}$, being formed. This substance is converted by nitrous fumes into *thiazolyl $\mu$-sulphide*,



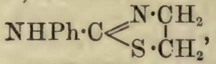
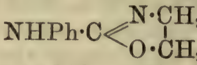
$$S\left(C<\begin{matrix}N{\cdot}CH_2\\ |\\ S{\cdot}CH_2\end{matrix}\right)_2,$$

which forms yellow crystals melting at 79—81°. Benzoic chloride converts vinylamine into *benzovinylamide*, $C_2H_3{\cdot}NHBz$; it is an oil, which solidifies in a freezing mixture, melts a little above 0° and is partially converted by distillation into $\mu$-phenyloxazoline,



$$C_2H_4<\genfrac{}{}{0pt}{}{O}{N}>CPh,$$

a tarry residue being left. Benzovinylamide combines very readily with the halogen acids. *Benzo-$\beta$-iodethylamide*, $CH_2I{\cdot}CH_2{\cdot}NHBz$, crystallises in yellowish plates, and melts at 110°. Bromethylbenzamide is converted by aniline into *benzophenylethylenediamine*, $NHPh{\cdot}CH_2{\cdot}CH_2{\cdot}NHBz$, which melts at 127°. The *platinochloride* melts and decomposes at about 205°. When boiled with benzoic chloride, it is converted into *dibenzophenylethylenediamine*, melting at 147·5°. *Benzophenylpropylenediamine*, $NHPh{\cdot}CHMe{\cdot}CH_2{\cdot}NHBz$, is obtained from $\beta$-bromopropylbenzamide in a similar manner. It crystallises in small needles, and melts at 110—111°.

Vinylamine unites with phenylic thiocarbimide to form vinylphenylthiocarbamide, $C_2H_3{\cdot}NH{\cdot}CS{\cdot}NHPh$, which crystallises in snow-white needles, and melts at 80°. When heated with fuming hydrochloric acid at 100°, it is converted into the isomeric n-*phenylethylene-ψ-thiocarbamide*,  $NHPh{\cdot}C{<}\begin{array}{l}N{\cdot}CH_2\\ \quad|\\ S{\cdot}CH_2\end{array}$, which forms compact, pointed prisms, and melts at 160°. *Vinylphenylcarbamide*, $C_2H_3{\cdot}NH{\cdot}CO{\cdot}NHPh$, is formed by the combination of vinylamine with phenylic carbimide; it crystallises in compact, lustrous needles melting at 82—83°. When it is heated with hydrochloric acid, it is converted into *β-chlorethylphenylcarbamide*, $C_2H_4Cl{\cdot}NH{\cdot}CO{\cdot}NHPh$, which crystallises in colourless scales, and melts at 124°; and this, when boiled with water, passes into n-*phenylethylene-ψ-carbamide*,  $NHPh{\cdot}C{<}\begin{array}{l}N{\cdot}CH_2\\ \quad|\\ O{\cdot}CH_2\end{array}$, which forms colourless, vitreous needles, and melts at 119—120°. β-Chlorethylphenylcarbamide reacts in a different manner with alcoholic potash, ethylenephenylcarbamide being produced. A. H.

**Partial Oxidation of some Secondary and Tertiary Amines.** By R. N. DE HAAS (*Rec. Trav. Chim.*, 1895, **14**, 166—184).—The object of this research was to follow the process of oxidation of certain secondary and tertiary amines when they are treated with an insufficient quantity of different oxidising agents. The quantity of oxidising agent was so adjusted that for one molecular proportion of a secondary amine there was one equivalent of available oxygen, and for one molecular proportion of a tertiary amine there was either one or two equivalents of available oxygen. The formation of either ammonia or nitrogen was not noticed, but the reactions may be expressed by the following equations.

$$\begin{aligned}NHR_2 &+ O = x\,NH_2R + (1-x)\,NHR_2 + \dots\\ NR_3 &+ O = x^1NH_2R + y^1NHR_2 + (1-x^1-y^1)NR_3 + \dots\\ NR_3 &+ 2O = x^2NH_2R + y^2NHR_2 + (1-x^2-y^2)NR_3 + \dots\end{aligned}$$

The author has endeavoured to determine the values of the unknown quantities $x$ and $y$ in these equations. The oxidising agents employed were potassium permanganate and potassium ferricyanide, and the following amines were investigated. Dimethylamine, diethylamine, dipropylamine, diisobutylamine, diamylamine, dibenzylamine, trimethylamine, triethylamine, and tripropylamine. The results are drawn up in two tables. A. R. L.

**Constitution of Hexamethylenetetramine.** By PAUL DUDEN and MAX SCHARFF (*Annalen*, 1895, **288**, 218—252; compare Abstr., 1895, i, 325).—Hexamethylenetetramine has been represented by numerous formulæ, and the author advocates a special expression, which consists of a symmetrically constructed tetrahedron having a nitrogen atom at each apex and a $CH_2$ group situated medially on each edge.

When dinitrosopentamethylenetetramine is suspended in cold water and agitated with sodium amalgam, diamidopentamethylenetetramine is produced, but the substance has not been isolated. On adding benzaldehyde to the liquid, however, *dibenzylidenediamidopentamethylenetetramine*, $C_5H_{10}N_2(N\cdot N{:}CHPh)_2$, is formed; it crystallises from alcohol in long, silky needles, exhibiting feebly green fluorescence, and melts at 226—227°. Boiling concentrated alkalis are without action on the substance, but it dissolves in cold, dilute acids, giving rise to formaldehyde, ammonia, hydrazine, and benzaldehyde.

*Diorthohydroxybenzylidenediamidopentamethylenetetramine* is obtained by adding salicylaldehyde to a solution containing the base; it crystallises from chloroform and ether in lustrous, white needles, and melts at 213°. It dissolves in alkalis, and is resolved into formaldehyde, ammonia, hydrazine, and salicylaldehyde by warm mineral acids.

*Dimetanitrobenzylidenediamidopentamethylenetetramine* is obtained from metanitrobenzaldehyde and the base; it crystallises from alcohol in lustrous, golden yellow needles, and melts at 134°.

*Dicinnamylidenediamidopentamethylenetetramine* crystallises from alcohol in pale yellow lustrous leaflets, and melts at 207°.

Reduction of trinitrosotrimethylenetriamine with sodium amalgam gives rise to a liquid containing triamidotrimethylenetriamine. The *triorthohydroxybenzylidene* derivative of this base crystallises from a mixture of chloroform and ether in long, white needles, and melts at 139—140°.

When a freshly prepared solution of diazobenzene chloride is added to well cooled, aqueous hexamethylenetetramine, a *compound*, $C_{17}H_{20}N_8$, is formed, which crystallises from benzene in yellowish-brown leaflets, and melts and decomposes at 228°. It is indifferent towards boiling alkalis, but when treated with dilute acids it yields nitrogen, ammonia, aniline, and formaldehyde. No evolution of gas attends the dissolution of ice-cold concentrated hydrochloric acid, the diazobenzene residue being eliminated.

*Bisparanitrodiazobenzenepentamethylenetetramine*,

$$C_5H_{10}N_2(N\cdot N{:}N\cdot C_6H_4\cdot NO_2)_2,$$

is obtained by mixing diazotised paranitraniline with hexamethylenetetramine at the temperature of melting ice, formaldehyde being eliminated. It dissolves with great difficulty in common solvents, but crystallises from hot ethylenic bromide in yellow needles, and melts and decomposes at 244°; it is indifferent towards boiling alkalis, but is resolved by dilute acids into nitrogen, ammonia, paranitraniline, and formaldehyde.

*Bismetanitrodiazobenzenepentamethylenetriamine* crystallises from a mixture of alcohol and chloroform in lustrous, yellowish-green plates, and melts, evolving gas, at 184°; nitrogen, ammonia, metanitraniline, and formaldehyde are formed under the influence of dilute acids.

*Sodium pentamethylenetetraminebisdiazobenzenesulphonate*,

$$C_{17}H_{18}N_8S_2O_6Na_2 + 6H_2O,$$

is only sparingly soluble in cold, but readily in hot, water; a portion of the water is given off at 100°, whilst above this temperature the salt becomes yellow and decomposes. The *silver* salt is amorphous, and the *copper* and *nickel* salts crystallise in minute needles; the *barium* salt, containing $3H_2O$, becomes anhydrous at 100°.

When aqueous hexamethylenetetramine is agitated with soda and benzoic chloride, two compounds are formed, one of which, dissolving in ethylenic bromide, consists of the *tribenzoyl* derivative of trimethylenetriamine; it melts at 220—221°, and when gently heated yields formaldehyde, ammonia, and benzoic acid. The second product, which does not dissolve in ethylenic bromide, is the *tribenzoyl* derivative of diamidodimethylamine; it crystallises in rhombohedra, and melts at 266—267°, yielding the same products as the foregoing substance when treated with mineral acids. M. O. F.

**Reactions of Formaldehyde.** By T. H. Lee (*Chem. News*, 1895, **72**, 153—154).—Formaldehyde reduces permanganate immediately, and is itself oxidised to carbonic anhydride and water; it also reduces potassium ferricyanide, hot Fehling's solution, and cold alkaline mercuro-potassium iodide, although neither ammoniacal copper sulphate nor mercuric chloride is affected in this manner by it. It deepens the colour of hot ferric chloride, and the solution, after cooling and re-heating, yields with ammonia a precipitate of basic ferric formate. Formaldehyde precipitates silver from its ammoniacal solution, both in the specular and pulverulent forms.

D. A. L.

**Organo-metallic Compounds.** By Ernst Beckmann and G. Schliebs (*Annalen*, 1895, **289**, 71—90; compare Abstr., 1892, 169).—The authors have endeavoured to ascertain the molecular weight of the sodium derivatives of certain ketones and alcohols by the ebullioscopic method. Examining camphor, menthone, deoxybenzoïn, and acetophenone, dissolved in ether or benzene, they find that the sodium derivatives of these compounds appear to have molecular weights amounting to three or four times the value calculated from their empirical formulæ; the determinations are not in agreement with definite chemical expressions, being appreciably dependent on the nature of the solvent, and the authors regard it as probable that a state of equilibrium exists between the dissociating action of the solvent and the tendency to associate exhibited by the molecules of the sodium derivatives. The sodium derivative of menthol is bimolecular, whilst ethylic and isopropylic alcohols, dimethylethylcarbinol, and phenol yield compounds of simple molecular structure; the sodium derivatives of ethylic acetoacetate and ethylic malonate are also unimolecular in alcoholic solution.

The volume of hydrogen liberated on adding sodium to a solution of ethylic acetoacetate or ethylic malonate in ether is in exact agreement with the amount required by theory; when acetone is treated in this way, a quantity amounting to 4·5 per cent. of the available hydrogen is liberated (compare Freer, Abstr., 1894, i, 65).

M. O. F.

**Behaviour of Thioacetic acid with Salt Solutions.** By N. Tarugi (*Gazzetta*, 1895, **25**, i, 341—352; compare Schiff and Tarugi, Abstr., 1895, ii, 84).—After washing with carbon bisulphide to remove free sulphur, the white precipitate obtained on adding thioacetic acid to solutions of mercuric chloride in the cold, is found to be *mercuric chlorosulphide*, $2HgS,HgCl_2$, not mercuric thioacetate as previously stated; it is an amorphous powder, soluble only in nitrohydrochloric acid. If mercuric nitrate is employed in place of the chloride, a white precipitate of *mercuric nitrosulphide*, $2HgS,Hg(NO_3)_2$, is deposited; this is a white, amorphous powder, which is blackened by soda or ammonia, and is soluble in nitrohydrochloric acid, but not in other acids. *Mercuric thioacetate*, $Hg(SAc)_2$, therefore, does not seem to have been previously obtained; it may be prepared by slowly adding thioacetic acid to alcoholic mercuric acetate in the cold, when a white precipitate, immediately changing to minute, transparent, yellow crystals, is deposited. This, on washing with carbon bisulphide and crystallising from chloroform, is obtained in beautiful, white scales; it is soluble in hot benzene or chloroform, and, on treatment with concentrated nitric acid or hot hydrochloric acid, yields the nitrosulphide or nitrochloride described above, whilst, with sulphuric acid, it yields the double *compound*, $3HgS,HgSO_4$. The thioacetate is converted into mercuric sulphide by ammonium sulphide, or by hot potash or soda, whereas hot ammonia gives rise to the acid *compound*, $Hg_2SH_2NOAc$. Mercuric thioacetate is soluble in nitrohydrochloric acid, and is reduced to mercury by stannous chloride. It is accompanied in its preparation by a basic *thioacetate*, $HgO,Hg(SAc)_2$, which can be separated by taking advantage of its insolubility in hot chloroform or benzene; it is a red, amorphous powder, insoluble in nitric or hydrochloric acid, but soluble in nitrohydrochloric acid.

On adding thioacetic acid to a copper salt in cold, neutral solution, a green precipitate is deposited which rapidly blackens during filtration; the filtrate slowly deposits red flocks of *cupric thioacetate*, $Cu(SAc)_2$, which is not affected by air or light, is soluble in nitric acid, and is converted into the sulphide by hydrochloric acid, dilute sulphuric acid, ammonia, soda, or ammonium sulphide.

Cadmium salts in cold solution yield a precipitate of *cadmium thioacetate*, $Cd(SAc)_2$, with thioacetic acid; it is a white, amorphous powder, soluble in mineral acids, and is converted into the sulphide by ammonia or ammonium sulphide.

On adding thioacetic acid to solutions of silver salts, a red precipitate is obtained which soon changes into the black silver sulphide; it is probably *silver thioacetate*.

A mixture of *lead thioacetate*, $Pb(SAc)_2$, and sulphur is deposited on adding thioacetic acid to neutral lead solutions; the new salt is a white crystalline substance which is converted into the sulphate by nitric acid, and into sulphide by ammonia, soda, or ammonium sulphide. Very dilute solutions of lead chloride give, in the cold, a red precipitate of *lead chlorosulphide*, $PbCl_2,3PbS$, from which boiling water extracts lead chloride. W. J. P.

**Synthesis by means of Ethylic Cyanacetate.** By C. TIMOTHÉE KLOBB (*Compt. rend.*, 1895, **121**, 463—465).—When ethylic or methylic α-cyan-β-benzoylpropionate is mixed, in molecular proportion, with potassium hydroxide in 5 per cent. solution, and the mixture is acidified at once with sulphuric acid, and extracted with ether, *cyanphenacylacetic acid* (*α-cyan-β-benzoylpropionic acid*),

$$COPh{\cdot}CH_2{\cdot}CH(CN){\cdot}COOH + H_2O,$$

is obtained. It crystallises from hot water in white, nacreous plates which melt at 69°, lose their water in a dry vacuum, and then melt at 99—100°. The sodium salt crystallises with $3H_2O$ in prisms very soluble in water and alcohol; the silver salt is white and insoluble; the phenylhydrazine compound melts at 113°. When boiled for a long time with a large excess of potassium hydroxide, cyanphenacylacetic acid yields phenacylacetic acid, $COPh{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, which melts at 116°, and is identical with the β-benzoylpropionic acid of Kues and Paal. *Methylic α-cyano-β-benzoyl-α-methylpropionate* forms slender needles which melt at 113°; *ethylic α-cyano-β-benzoyl-α-ethylpropionate* crystallises from carbon bisulphide in large, rhombic prisms which melt at 64°; *methylic α-cyano-β-benzoyl-α-benzylpropionate* melts at 133—134°. Attempts to displace the hydrogen by benzoyl were unsuccessful, a result analogous to that obtained by Haller with alkylic cyanacetoacetates.

Ethylic sodiocyanacetate and chloracetone in presence of absolute alcohol, yield *ethylic cyanacetonylacetate* (*α-cyan-β-acetylpropionate*), an amber-coloured liquid, which boils at 160—171° under a pressure of 24 mm.; sp. gr. = 1·100 at 16°. It dissolves in alkalis and in concentrated hydrochloric acid; its phenylhydrazone forms white needles which melt at 144°. Methylic sodiocyanacetate in presence of methylic alcohol yields the corresponding methyl compound which boils at 159—166° under a pressure of 26 mm.; sp. gr. = 1·148 at 16°. Its phenylhydrazone melts at 137—138°. C. H. B.

**Action of Sulphur on Unsaturated Aliphatic Compounds.** By JULIUS ALTSCHUL (*Zeit. angw. Chem.*, 1895, 535—542).—The first part of this paper consists of a *résumé* of the work done by Henriques (*Chem. Zeit.*, 1893, 636), Weber (*ibid.*, 1894, 112), Anderson (*Annalen*, **63**, 370), Benedikt and Ulzer (*Monatsh.*, 1887, 208).

Saturated fatty acids, such as stearic acid, when heated with sulphur for some time a little above their melting points, are not appreciably acted on; in order to decompose such an acid, it must be heated with sulphur to at least 200°. Hydrogen sulphide is then evolved and substitution products, resembling those obtained by Benedikt, are formed. An unsaturated acid, such as oleïc acid, behaves quite differently; when heated with 10 per cent. of sulphur for some time at 130—150°, complete solution ensues and chemical combination takes place without the evolution of hydrogen sulphide. All unsaturated compounds behave in exactly the same manner with sulphur, and within the same range of temperature. The author has proved that combination with sulphur does actually take place, since the products formed by the action of sulphur on fatty oils, when hydrolysed with alkali, yield soaps, and these when acidified yield acids which contain sulphur chemically combined; the hydrolysis is best carried out at low temperatures with alcoholic potash, as when hydrolysed at fairly high temperatures, hydrogen sulphide is eliminated, and salts of acids free from sulphur are obtained (compare Henriques).

The sulphur additive compounds, just like the oxidation products, of the fats, unite with sulphur chloride, $S_2Cl_2$. The fatty oils which are most readily oxidised, namely, those which most readily form additive compounds with oxygen, are also the compounds which most readily unite with sulphur. Sulphur chloride does not readily unite with those sulphur additive compounds which are difficult to prepare.

The nature of the sulphur additive compounds varies greatly with the nature of the oil and the temperature at which the operation is carried out. Oleïc acid apparently unites with 1 atom of sulphur at moderate temperatures, whereas many glycerides form varying products (probably mixtures) which are largely influenced by the temperature at which the action takes place. J. J. S.

**Thiorufic and Thiocarbacetoacetic acid.** By OSKAR EMMERLING (*Ber.*, 1895, **28**, 2882—2888).—The analysis and cryoscopic determination of the molecular weight of thiorufic acid lead to the formula $C_{21}H_{26}S_6O_8$, instead of the simpler formula, $C_{10}H_{14}S_3O_4$, which was ascribed to this substance by Oppenheim and Norton (*Ber.*, **10**, 701); the salts have corresponding formulæ, the sodium salt being $C_{21}H_{26}Na_2S_6O_8$. When this sodium salt is treated in the cold with aqueous soda, hydrolysis takes place, and a new *acid* is formed, which is very readily soluble in water, and melts at about 173°. This substance has the formula $C_{15}H_{16}S_6O_8$, and is pentabasic, the *barium salt* having the formula $(C_{15}H_{11}S_6O_8)_2Ba_5$. The authors propose to give the name *thiorufic acid* to this new compound, the original acid of Oppenheim and Norton being known as *etherthiorufic acid.*

Ethylic thiocarbacetoacetate was also first prepared by Oppenheim and Norton, who ascribed to it the constitution $CS{:}CAc{\cdot}COOEt$. This formula is confirmed by the fact that when the substance is heated in alcoholic solution with lead oxide, malonic acid is formed, lead sulphide and acetic acid being also produced. Ethylic thiocarbacetoacetate yields a *dibromo-derivative*, which crystallises in thick, yellow needles, and melts at 171°, as well as a *tribromo-derivative*, which crystallises in lustrous yellow plates melting at 180°. The latter of these also yields malonic acid when it is treated with lead oxide, and this reaction proves the presence of a methyl group in the original substance. In the preparation of ethylic thiocarbacetoacetate, a small amount of ethylic malonate, which is probably derived from a partial decomposition of this compound, is always produced.

A. H.

**Action of Sodium Hydroxide on Allylmalonic, Allylacetic, and Ethylidenepropionic acid.** By JOHN G. SPENZER (*J. Amer. Chem. Soc.*, 1895, **17**, 1—32).—The greater part of this work has been previously published (compare Fittig and Spenzer, Abstr., 1895, i, 204). It is shown that $\gamma\delta$-unsaturated acids behave very differently from $\beta\gamma$-acids when boiled with sodium hydroxide solution. Allylmalonic acid is not acted on when treated in this way, and allylacetic acid yields only a trace of an acid whose barium salt is soluble in alcohol, but the exact composition of which could not be determined. Sodium ethylidenepropionate, on the other hand, is readily converted into sodium propylideneacetate. In the preparation of ethylidenepropionic acid by the destructive distillation of methylparaconic acid, the distillate contains valerolactone, methylcitraconic acid, methylitaconic acid, and unaltered methylparaconic acid. The author gives methods for the separation of each constituent.

J. J. S.

**Action of Zinc and Ethylic Bromisobutyrate on Acetone. Synthesis of Tetramethylethylenelactic acid.** By SERGIUS REFORMATSKY and B. PLESCONOSSOFF (*Ber.*, 1895, **28**, 2838—2841).—Ethylic bromisobutyrate and acetone, in molecular proportion, are added to zinc, the mixture is cooled with water, and after a week is heated at 60—70° during two hours, water is added, the liquid is acidified with sulphuric acid, and the oil removed, washed, dried, and fractionated. The first portion consists chiefly of ethylic isobutyrate, the second portion (b. p. 150—200°) when redistilled, yields *ethylic β-hydroxytetramethylpropionate*, $OH\cdot CMe_2\cdot CMe_2\cdot COOEt$ (tetramethylethylenelactate), which is a thick, yellow liquid, boiling at 196—197°; it has a pleasant odour, and is insoluble in water. The free *acid*, prepared by hydrolysis of the ethylic salt with barium hydroxide, crystallises in plates, melts at 152—153°, previously decreasing in volume, and boils and in part decomposes at 192—193°. By the action of sulphuric acid, dimethylisopropylcarbinol and tetramethylethylene are formed; hydriodic acid yields tetramethylethylic iodide. The yield of acid is 25 per cent. of the theoretical. The *barium salt* forms stellate crystals which become pulverulent when dried. The *calcium salt* crystallises in plates, the *silver salt* in short, lustrous prisms, and the *lead salt* in tetragonal prisms; the *sodium* and *zinc salts* have also been prepared; all are readily soluble in water.

J. B. T.

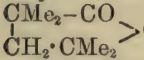
**Action of Zinc and Ethylic Bromisobutyrate on Isobutaldehyde. Synthesis of Secondary β-Hydroxy-acids.** By SERGIUS REFORMATSKY (*Ber.*, 1895, **28**, 2842—2847).—It has been previously shown (Abstr., 1887, 717) that ethylic chloracetate and zinc yield, with ketones, tertiary β-hydroxy acids, but no corresponding compounds are formed with aldehydes, the action proceeding so slowly that the latter are in part oxidised and in part undergo condensation. Ethylic bromisobutyrate reacts more quickly, and, with aldehydes, yields secondary β-hydroxy-acids. The ethylic salt and aldehyde are mixed in molecular proportion, and added to the zinc in a reflux apparatus, the flask is allowed to remain in a cold water bath during 7—9 days, then heated at 60—70° for 1—3 hours; after 24 hours, the product is treated successively with water and dilute sulphuric acid, and the oily layer removed and purified.

*Ethylic β-hydroxy-α-dimethyl-β-isopropylpropionate*,

$$CHMe_2\cdot CH(OH)\cdot CMe_2\cdot COOEt,$$

is a yellow, viscid liquid with a pleasant odour, and is insoluble in water; it boils at 160° (140 mm.) and at 221—222° (738·5 mm.).

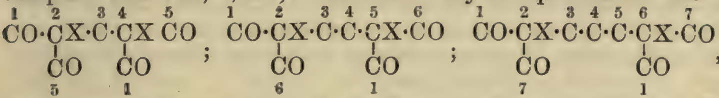
The acid crystallises in lustrous prisms, melts at 92°, and is optically inactive; at 19°, 2·03 parts dissolve in 100 of water. The yield is 58 per cent. of the theoretical. The molecular weights of both compounds were determined by the cryoscopic method in benzene. The *salts* are all readily soluble in water with the exception of the *copper* compound; the *calcium salt* crystallises in prisms. The acid (m. p. 111—112°) prepared by Hantzsch and Wohlbrück by the action of sodium on ethylic isobutyrate is diisopropyloxalic acid, not the above hydroxydimethylisopropylpropionic acid, but the latter has been previously obtained by Fossek by oxidising the aldol condensation product of isobutaldehyde. When distilled with dilute sulphuric acid (1 : 5), the above acid yields carbonic anhydride, dimethylisopropylethylene, and a neutral compound, which is probably a *lactone*,



$\begin{array}{l}\mathrm{CMe_2{-}CO}\\ \vert\\ \mathrm{CH_2\cdot CMe_2}\end{array}\!\!>\mathrm{O}$; it boils at 209—211°, melts at 52·5—53·5°, and its formation is probably preceded by that of the unsaturated $\beta\gamma$-acid. By the action of hydriodic acid on the propionic acid, the same lactone is formed together with heptylic iodide (?) in small quantity.

J. B. T.

**Formation of Carbon Chains. II. Conjugated Ethereal Malonates.** By Carl A. Bischoff (*Ber.*, 1895, **28**, 2824—2835; compare this vol., i, 84).—Hitherto only compounds of the types



$\overset{1}{\mathrm{CO}}\cdot\underset{\underset{5}{\mathrm{CO}}}{\overset{2}{\mathrm{C}}}\mathrm{X}\cdot\overset{3}{\mathrm{C}}\cdot\underset{\underset{1}{\mathrm{CO}}}{\overset{4}{\mathrm{C}}}\mathrm{X}\;\overset{5}{\mathrm{CO}}$; $\overset{1}{\mathrm{CO}}\cdot\underset{\underset{6}{\mathrm{CO}}}{\overset{2}{\mathrm{C}}}\mathrm{X}\cdot\overset{3}{\mathrm{C}}\cdot\overset{4}{\mathrm{C}}\cdot\underset{\underset{1}{\mathrm{CO}}}{\overset{5}{\mathrm{C}}}\mathrm{X}\cdot\overset{6}{\mathrm{CO}}$; $\overset{1}{\mathrm{CO}}\cdot\underset{\underset{7}{\mathrm{CO}}}{\overset{2}{\mathrm{C}}}\mathrm{X}\cdot\overset{3}{\mathrm{C}}\cdot\overset{4}{\mathrm{C}}\cdot\overset{5}{\mathrm{C}}\cdot\underset{\underset{1}{\mathrm{CO}}}{\overset{6}{\mathrm{C}}}\mathrm{X}\cdot\overset{7}{\mathrm{CO}}$, have been prepared from ethylic alkylsodiomalonates and methylenic iodide, ethylenic bromide, and trimethylenic bromide respectively. The difficulty of obtaining methylenic bromide in quantity has, for the present, restricted the quantitative investigation of the reaction to the second and third type; the results are in complete accord with the dynamical theory which indicates that the linking should be effected more readily in the latter (position 1—7) than in the former (position 1—6) case.

(1) *Ethylenic bromide with ethylic alkylmalonates.*—The malonate was mixed with alcoholic sodium ethoxide, and ethylenic bromide added; after boiling during 10 hours more ethylenic bromide was added, the boiling continued during seven hours, and this treatment repeated until the liquid was no longer alkaline. The normal compound was never formed in any considerable quantity, the products being mixtures of the original ethylic salt and the bromo-derivative, $\mathrm{CX(COOEt)_2\cdot CH_2\cdot CH_2Br}$. A portion of the ethylic salts undergo hydrolysis, and the sodium derivatives thus formed dissolve in the crude product and decompose during the distillation, forming gaseous substances; this was most marked in the case of ethylic isobutylmalonate. The following ethylic alkylmalonates were employed: Methyl-, ethyl-, propyl-, isopropyl-, isobutyl, isoamyl-, and allyl-, Experiments were also made with mono-, di-, and tri-methylethylenic bromides; in no case is the reaction normal, but, with trimethylethylenic bromide, for example, the ethylic malonates combine, and trimethylethylene is formed.

(2) *Trimethylenic bromide with ethylic sodiomalonate and ethylic sodiomethylmalonate respectively.*—In both these cases, normal products were obtained and identified by analysis and observation of their boiling point. The substitution of allylic tribromide for trimethylenic bromide gives rise to abnormal products. From carbon tetrachloride and ethylic sodiomalonate, a compound containing only two malonyl radicles was obtained. Chabrié has described a compound with four radicles, $C[CH(COOEt)_2]_4$, but a repetition of his experiments does not confirm the statement; ethylic ethanetetracarboxylate and an orange-yellow *sodium compound*,

$$(COOEt)_2C:C:C(COONa)COOEt \text{ or } (COOEt)_2C:C(OEt)\cdot CNa(COOEt)_2,$$

are formed (compare Zelinsky and Doroschewsky, Abstr., 1895, i, 129).

Experiments with ethylic sodio- and disodio-malonate and tetrachloro-, and tetraiodoethylene show that the action proceeds according to the equation $4CHNa(COOEt)_2 + C_2I_4 = 4NaI + C_2H_2 + CH(COOEt)_2\cdot CH(COOEt)_2 + C(COOEt)_2:C(COOEt)_2$; the quantity of acetylene formed is practically the same from both the sodium compounds, and is about twice as great as from an equivalent quantity of sodium ethoxide; the substitution of xylene for alcohol as the solvent has little influence on the reaction. Negative results were obtained with the two sodium compounds and hexachlorethane and hexachlorobenzene. Full experimental details are given in the paper.

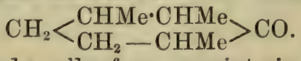
J. B. T.

**Trimethylpimelic acid.** By NICOLAI D. ZELINSKY and A. REFORMATZKY (*Ber.*, 1895, **28**, 2943—2945).—A mixture of ethylic cyanopropionate and dibromobutane, $CHMeBr\cdot CH_2\cdot CH_2Br$ (Demjanow, Abstr., 1895, i, 191), was treated with sodium ethoxide; the resulting *ethylic dicyanotrimethylpimelate*,

$$COOEt\cdot CMe(CN)\cdot CHMe\cdot CH_2\cdot CH_2\cdot CMe(CN)\cdot COOEt,$$

boils at 232—233° under 20 mm. pressure. When it is boiled with sulphuric acid, it becomes hydrolysed, and loses carbonic anhydride, and *trimethylpimelic acid*,

$$COOH\cdot CHMe\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot COOH,$$

is obtained; this boils at 213—215° under 15 mm. pressure. When the calcium salt is distilled with excess of calcium hydroxide, that fraction of the distillate which boils at 190—191° consists mainly of *trimethylketohexamethylene*,  $CH_2<\begin{matrix}CHMe\cdot CHMe\\ CH_2-CHMe\end{matrix}>CO$. This has a sp. gr. = 0·9129 at 18°/4°, and smells of peppermint; in moist ethereal solution, it is reduced by sodium to the *alcohol*, which boils at 193—195° under 747 mm. pressure, has a sp. gr. = 0·9119 at 17°/4°, and smells like menthol.

C. F. B.

**Alloisomerism.** By ARTHUR MICHAEL (*J. pr. Chem.*, 1895, [2], **52**, 289—325; compare Abstr., 1891, 1184; 1893, i, 142, 144).—

This, and the four succeeding papers, are devoted to the exposition of facts and theories which are at variance with van't Hoff's stereochemical hypothesis and with Wislicenus's arguments in support thereof.

The best methods for obtaining bromine additive compounds of unsaturated acids are dealt with. *Citradibromopyrotartaric anhydride*, $C_5H_4Br_2O_3$, is a yellowish oil, and is prepared by exposing a mixture of the calculated quantities of citraconic anhydride and bromine to sunlight.

Bromomaleïc acid was prepared by three methods, each of which is described, and was found to be identical in each case, and Petri's conclusion with respect to Kekulé's results (Abstr., 1879, 373) is confirmed; the acid melts at 136—138°, not 128° (*loc. cit.*). A similar investigation into the methods for preparing bromofumaric acid led to a similar conclusion; the acid melts at 185—186°, not 177—178°. Details of the behaviour of the lead and silver salts of both these acids are given. By taking advantage of the difference in solubility of the hydrogen potassium salts of these acids (100 parts of water at 14° dissolve 4·04 parts of the bromofumarate and 23·8 parts of the bromomaleate), it was shown that when dibromosuccinic acid is boiled with water (*loc. cit.*), about 2—3 per cent. of bromofumaric acid is produced, together with bromomaleïc acid, but the converse production of bromomaleïc acid together with bromofumaric acid, when isobromosuccinic acid is boiled with water, could not be proved.

According to the generally accepted configuration for bromomaleïc and bromofumaric acids, the former should lose hydrogen bromide more readily than the latter, these elements being plane-symmetrical in bromomaleïc acid; experiments were accordingly made with chloromaleïc and chlorofumaric acids, in which equal weights were treated with a slight excess of caustic potash under the same conditions, and the amount of potassium chloride formed was determined in each case after the lapse of a certain time. It was found that at 10°, in the course of 48 hours, about 48 times as much hydrogen chloride was eliminated from chlorofumaric acid as from chloromaleïc acid under similar conditions; even at 100°, this difference is still to be noticed after the lapse of 15 minutes, the ratio of decomposability being, however, much smaller, namely, 1 : 1·2 instead of 1 : 48. In the same way, it was shown that in the course of 24 hours at 10°, bromofumaric acid lost 18 times as much hydrogen bromide as bromomaleïc acid did. If the facility with which halogen hydride is eliminated from these acids is to be regarded as indicative of plane-symmetry of structure, then the above experiments show that bromofumaric acid is plane-symmetrical.

Another argument advanced by Wislicenus for plane-symmetry in an acid is that such a configuration must be indicated by easy elimination of carbonic anhydride from the salts of the acid. Accordingly, a comparison was made between the amount of carbonic anhydride lost by equal weights of silver bromofumarate and silver bromomaleate respectively, when heated at 100° in aqueous solution, and it was found that in two hours silver bromomaleate lost 4·3 times as much carbonic anhydride as silver bromofumarate did. When the same method was applied to silver bromomesaconate and silver bromocitraconate, it was found that in 16 hours at 105° the bromomesaconate had lost 3·68 per cent. of carbonic anhydride, and the bromocitraconate 7·11 per cent.

Bromomaleïc acid yields fumaric acid when reduced by zinc dust, even in absence of alkalis, which are known to partially convert maleïc into fumaric acid; so, also, bromocitraconic acid yields mesaconic acid, even in the absence of alkalis.

Bandrowski's statement (*Ber.*, 1882, **15**, 2695) that chlorofumaric acid is obtained when hydrogen chloride reacts with acetylenedicarboxylic acid is confirmed; this is contrary to Wislicenus's interpretation of van't Hoff's hypothesis.

By adding a strong solution of potassium thiocyanate to one of maleïc acid, fumaric acid is precipitated; but this conversion does not admit of a similar interpretation to that applied by Wislicenus to the conversion effected by mineral acids (*Räuml. Anord.*, 29). Isodibromosuccinic acid is converted into dibromosuccinic acid when heated with a saturated solution of hydrogen bromide at 100° in a sealed tube. A. G. B.

**Relative Ease of Elimination of Carbonic Anhydride from the Silver Salts of the β-Chlorocrotonic acids.** By ARTHUR MICHAEL and T. H. CLARK (*J. pr. Chem.*, 1895, [2], **52**, 326—330).—Silver β-chlorallocrotonate is decomposed with elimination of carbonic anhydride more easily than is silver β-chlorocrotonate. β-Chlorallocrotonic acid yields β-chlorocrotonic acid when heated with hydrochloric acid. Ethylic dibromofumarate loses halogen more easily than ethylic dibromomaleate does. A. G. B.

**Alloisomerism.** By ARTHUR MICHAEL and GEORG TISSOT (*J. pr. Chem.*, 1895, [2], **52**, 331—343).—It has been shown already (Abstr., 1893, i, 142) that dichlorosuccinic acid yields chlorofumaric acid when it loses hydrogen chloride; when heated with acetic anhydride, however, it yields chloromaleïc acid, and this, by reduction with zinc, is converted into fumaric acid. When sodium dichlorosuccinate is heated in aqueous solution for half an hour, it is converted into sodium chloromaleate, a result which renders it possible that when excess of alkali is used (*loc. cit.*), the production of chlorofumaric acid is due to the further action of this alkali on chloromaleïc acid.

Dichlorosuccinic acid yields both racemic acid and inactive tartaric acid when its halogen atoms are replaced by hydroxyl groups, in this resembling dibromosuccinic acid.

Bromomesaconic acid (Abstr., 1894, i, 444) melts at 217—218°, and dissolves easily in water, alcohol, acetic acid, and ethylic acetate, but only very sparingly in benzene and chloroform.

Mesadichloropyrotartaric acid yields the same products when heated with water as are obtained from citradichloropyrotartaric acid under the same conditions (Abstr., 1893, i, 142). Citradichloropyrotartaric acid does not yield the so-called hydroxycitraconic acid when heated with baryta water (Morawski, *J. pr. Chem.*, [2], **11**, 446).

The behaviour of xeronic anhydride and of aconitic acid and its

ethereal salts towards halogens was studied, without any very definite results.
A. G. B.

**The Laws of Alloisomerism and their Employment in Classifying Unsaturated Organic Compounds.** By ARTHUR MICHAEL (*J. pr. Chem.*, 1895, [2], **52**, 344—365.—The following rules constitute a summary of the modes of formation, reactions, and stability of alloisomeric compounds as elucidated by the experiments of the author and his fellow-workers.

1. If two unsaturated monhalogen acids are obtainable from one saturated $\alpha\beta$-dihalogen acid, they will be alloisomeric $\alpha$-derivatives.

2. The maleinoïd modifications of unsaturated compounds are more easily soluble, of lower melting point, and more volatile than the corresponding fumaroïd modifications.

3. Of two halogen-free, alloisomeric, unsaturated acids, that of lower melting point will be converted into the fumaroïd modification, of higher melting point, by being heated with water, mineral acids, or halogens.

4. The lower melting, maleinoïd form of an $\alpha\beta$-unsaturated $\alpha$-halogen acid passes into the higher melting, fumaroïd form when heated, and when under the influence of mineral acids.

5. Fumaroïd derivatives from $\alpha\beta$-unsaturated halogen-free monobasic acids of the ethylene series, formed by the replacement of $\beta$-hydrogen by a negative atom or radicle (halogen or carboxyl), are converted by heat, either entirely or in part, into the corresponding maleinoïd modifications.

6. The maleinoïd modifications referred to in 5, are converted, entirely or partly, into the fumaroïd modifications when heated with mineral acids.

7. If the halogen is present in the $\alpha$- as well as in the $\beta$-position in alloisomeric $\alpha\beta$-unsaturated ethylene compounds, the influence of each position is exerted, and such compounds are partially converted into each other when heated.

8. The addition of 1 mol. of halogen hydride to an $\alpha\beta$-unsaturated acid of the acetylene series directly produces, either entirely or in great part, a $\beta$-halogen acid of the higher melting fumaroïd form.

9. The higher melting, fumaroïd modification of two alloisomeric, $\alpha\beta$-unsaturated, $\alpha$- or $\beta$-halogen acids of the acetylene series yields halogen hydride more easily than does the lower melting maleinoïd modification.

10. A mixture of two alloisomeric additive products is formed when bromine is added to an acetylene derivative containing a negative radicle in the place of hydrogen, but the fumaroïd modification will be directly formed in the larger proportion.

11. Of two alloisomeric $\alpha\beta$-dibromethylene derivatives, the fumaroïd modification yields a halogen-free acetylene derivative by loss of bromine more easily than the maleinoïd modification does.

12. By the addition of bromine to both modifications of an $\alpha\beta$-unsaturated $\alpha$-bromo-acid, the same unsaturated tribromo-acid is obtained.

13. Both alloisomeric modifications of an $\alpha\beta$-unsaturated $\alpha$-halogen

fatty acid yield wholly, or in great part, the same halogen-free acid, namely, the higher melting fumaroïd modification, when the halogen is replaced by hydrogen.

14. The silver salts of alloisomeric, $\alpha\beta$-unsaturated $\beta$-halogen acids of the ethylene series are decomposed by water with formation of silver acetylide, or silver alkylacetylide, carbonic anhydride, and silver haloïd. This decomposition takes place more readily in the case of a maleinoïd form than in the case of a fumaroïd form.

15. By separation of halogen from the two modifications of a saturated $\alpha\beta$-dihalogen acid or its ethereal salt, the fumaroïd modification of the corresponding unsaturated acid, or its ethereal salt, is formed.

16. By the elimination of 1 mol. of hydrogen bromide from the product of the addition of bromine to a fumaroïd fatty acid of the ethylene series, there is produced, for the major part, a maleinoïd $\alpha$-bromo-acid; contrariwise, a fumaroïd bromo-acid is the chief product of a similar change in an allo-$\alpha\beta$-dibromo-acid. In the case of the corresponding chloro-acids, the elimination of hydrogen chloride yields a mixture of both $\alpha$ chloro-acids.

17. No generalisation is yet possible concerning the stability of saturated alloisomeric $\alpha\beta$-dibromo-fatty acids towards mineral acids.

18. Chlorine and bromine are not necessarily equivalent elements in an alloisomeric sense, so that the behaviour of a chlorinated derivative cannot be deduced from that of a brominated derivative.

19. Ring-formation is a periodic function of the chain-length.

20. The relative positiveness and negativeness of an unsaturated carbon atom is dependent on its absolute distance from the other atoms of the molecule, so that the "positive-negative rule" (Abstr., 1889, 1140) is applicable for the ascertainment of the position of such atoms.

A table of maleinoïd and fumaroïd modifications of $\alpha\beta$-unsaturated alloisomeric compounds is given, together with detailed examples of the foregoing rules.

The untenable character of the Wislicenus-van't Hoff configuration is then discussed. A. G. B.

**Alloisomerism: Remarks on the Work of Bischoff, Wislicenus, and van't Hoff.** By Arthur Michael (*J. pr. Chem.*, 1895, [2], **52**, 365—372).—A controversial paper.

**Influence of Substitution on the Course of the Reactions of Ketones.** By Pavel Iw. Petrenko-Kritschenko, L. Pissarschewsky, and M. Herschkowitsch (*Annalen*, 1895, **289**, 52—58).—In view of the attention which has been recently directed to the influence of substitution on chemical behaviour, the authors have investigated the action of phosphorus pentachloride on alkylic salts of substituted acetonedicarboxylic acids. It has been shown by von Pechmann, that towards this agent ethylic acetonedicarboxylate exhibits the behaviour of alkylic salts of normal ketonic acids, and the authors have found that the ethylic salts of mono- and di-methylacetonedicarboxylic acids, and of mono- and di-ethylacetonedicarboxylic acids are also vigorously attacked by phosphorous pentachloride. This agent acts on ethylic trimethylacetonedicarboxylate, whilst ethylic triethylacetonedicarboxylate is indifferent towards it, this difference in behaviour being due to the respective masses of the substituents.

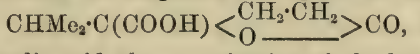
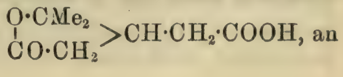
*Ethylic tetramethylacetonedicarboxylate* boils at 146—152°, under a pressure of 25 mm.; it is indifferent towards phosphorus pentachloride, which has no action on ethylic tetrethylacetonedicarboxylate.

Whilst the behaviour of ethylic acetoacetate towards phosphorus pentachloride is normal, derivatives containing one or two alkylic substituents undergo chlorination. M. O. F.

**Influence of Substitution on the Course of the Reactions of Ketones.** By Pavel Iw. Petrenko-Kritschenko and S. Ephrussi (*Annalen*, 1895, **289**, 58—61; compare the foregoing abstract).—Generation of heat marks the combination of phenylhydrazine with ethylic monomethylacetonedicarboxylate and ethylic monethylacetonedicarboxylate, action being less energetic in the case of the latter salt. The *hydrazone* of ethylic monomethylacetonedicarboxylate crystallises from dilute alcohol in lustrous plates, and melts at 129—130°; when hydrolysed with caustic soda, it yields the *hydrazone* of the acid, which melts and evolves carbonic anhydride at 168—169°, yielding a pyrazolone derivative. M. O. F.

**Action of Carbon Tetrachloride on Methylic Sodiomalonate.** By Nicolai D. Zelinski and A. Porchunow (*Ber.*, 1895, **28**, 2946—2947).—When carbon tetrachloride acts on methylic sodiomalonate, $CHNa(COOMe)_2$, in the presence of sodium methoxide, a substance is formed which melts at 136—137°. It appears to have the composition $OH{\cdot}C[CH(COOMe)_2]_3$. C. F. B.

**Dihydroxytrimethylglutaric acid.** By Nicolai D. Zelinski and L. Tschugaew (*Ber.*, 1895, **28**, 2940—2942).—Methyl acetylacetone, $CHMe(CMeO)_2$ (Dunstan and Dymond, Trans., 1891, 428), was converted by means of hydrocyanic acid into a *nitrile*, which yielded *dihydroxytrimethylglutaric acid*, $CHMe[CMe(OH){\cdot}COOH]_2$, when hydrolysed with hydrochloric acid in the cold. The nitrile melts at 124—125°. The acid melts at 83—84°, and easily loses 1 mol. of water, forming a *lactonic acid*, which melts at 119—120°; when distilled under atmospheric pressure, it yields a solid *dilactone*. It is remarkable that the lactonic acid very readily unites with water, re-forming the dihydroxy-acid. C. F. B.

**Isopropylglutolactonic acid; Constitution of Terpenylic acid.** By Rudolph Fittig and Adolf Wolff (*Annalen*, 1895, **288**, 176—191).—The authors' investigation having shown that isopropylglutolactonic acid,  $CHMe_2{\cdot}C(COOH)<\begin{matrix}CH_2{\cdot}CH_2\\ O\text{———}\end{matrix}>CO$, bears no resemblance to terpenylic acid, the constitution of the latter substance is probably represented by the formula  $\begin{matrix}O{\cdot}CMe_2\\ |\\ CO{\cdot}CH_2\end{matrix}>CH{\cdot}CH_2{\cdot}COOH$, an expression which was first advocated by Wallach, and has been recently supported by Schryver.

*βγ-Dibromisoheptoic acid*, $CHMe_2 \cdot CHBr \cdot CHBr \cdot CH_2 \cdot COOH$, is obtained by adding bromine to a solution of βγ-isoheptenic acid in carbon bisulphide, the operation being carried on in diffused daylight at 0° in absence of moisture; it melts at 102—103°, and crystallises in transparent, colourless plates belonging to the monosymmetric system, $a : b : c = 0{\cdot}732 : 1 : 0{\cdot}641$; $\beta = 67° 15'$. When heated during 24 hours with water in a reflux apparatus, the acid is converted into isoheptenolactone and hydroxyisoheptolactone (Abstr., 1895, i, 207), δ-dimethyllevulinic acid being formed at the same time (*loc. cit.*); the *calcium* salt of this acid contains $3\frac{1}{2}H_2O$, and the *silver* salt is indifferent towards light.

*Isopropylglutolactanic acid* is obtained by adding a concentrated solution of δ-dimethyllevulinic acid to finely powdered potassium cyanide, allowing the mixture to remain at the ordinary temperature during 24 hours, and adding concentrated hydrochloric acid while the liquid is kept cool with ice; it melts at 67—68°. The acid separates from a mixture of ether and petroleum in small, monosymmetric crystals; it is very soluble in water, but does not crystallise from the aqueous solution. The *barium* salt contains $2H_2O$, and crystallises in monosymmetric prisms; the *calcium* salt contains $2\frac{1}{2}H_2O$, and the *silver* salt is indifferent towards light and heat. The *amide* is an intermediate product formed in hydrolysing the cyanhydrin with hydrochloric acid; it crystallises from water in lustrous, transparent prisms belonging to the monosymmetric system; $a : b : c = 0{\cdot}7771 : 1 : 0{\cdot}76382$; $\beta = 54° 34'$.

When isopropylglutolactonic acid is heated with aqueous alkalis, salts of isopropylhydroxyglutaric acid are produced. The *barium* salt is anhydrous; the *calcium* salt contains $3H_2O$, and the *silver* salt is amorphous. M. O. F.

**Aconitic acid from Adonis vernalis.** By N. Orloff (*Chem. Centr.*, 1895, i, 202; from *Pharm. Zeit. Russ.*, **33**, 771).—*Adonis vernalis* gives better yields than either *Aconitum* or *Equisetum*. After several drops of concentrated lead acetate solution have been added to the aqueous extract, and the precipitate formed has been removed, excess of the reagent is added, and the precipitate collected, well washed, and decomposed by dilute sulphuric acid. The filtrate is concentrated, and extracted with ether; after evaporation of the ether, the aqueous solution of aconitic acid is decolorised by means of animal charcoal. J. J. S.

**Formation of Citric acid by the Oxidation of Cane Sugar.** By Edwin F. Hicks (*Chem. News*, 1895, **72**, 165—166).—Phipson dissolved a few grams of cane sugar in water, to which a few drops of sulphuric acid had been added, and poured in a rather strong solution of potassium permanganate; in a short time, at summer temperature, the solution became clear and colourless. When this was neutralised with ammonia and calcium chloride added, there was no precipitate in the cold, but, on heating, crystalline calcium citrate separated; with large quantities of permanganate, oxalic acid was also produced.

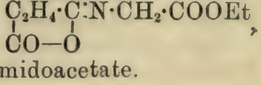
The author of the present note has repeated and also varied the experiment, using acid above and below 1 per cent.; with the former a precipitate is obtained both in cold and hot solution, but with the latter, only in the hot solution, the precipitate in all cases being calcium sulphate without a trace of organic acid. When nitric acid was used instead of sulphuric acid, no precipitate was obtained.

D. A. L.

**Citric and Tartaric acids from Cane Sugar.** By THOMAS L. PHIPSON (*Chem. News*, 1895, **72**, 190—191 and 257).—The failure of others to obtain citric acid from cane sugar (compare preceding abstract) is attributed by the author to the use of insufficient permanganate, of which a quantity not less than the weight of the sugar should be used; temperature and the character of the acid used are also stated to play an important part. Moreover, he finds that when a solution of equal weights of sugar, nitric acid, and potassium permanganate, after being left for 24 hours in the cold, is neutralised with calcium carbonate, a copious precipitate containing calcium tartrate is obtained, and the clear solution, on boiling, yields a further precipitate, which is calcium citrate. Saccharic acid and formic acid have also been obtained in these reactions by the author. D. A. L.

**Citric acid from Cane Sugar.** By ALFRED B. SEARLE and ARNOLD R. TANKARD (*Chem. News*, 1895, **72**, 235, 268).—Hicks' (see above) results confirm previous work of the authors, who have since endeavoured to obtain citric acid in accordance with the method set forth by Phipson (preceding abstract), using equal weights of cane sugar, nitric acid (sp. gr. 1·42), and permanganate, the latter being added in strong solution. They did not obtain citric acid, but when sulphuric acid was used instead of the nitric acid, calcium sulphate was obtained as in their previous experiments. D. A. L.

**Hydrazides of Substituted Amido-acids; Fumarylhydrazide.** By RUDOLF RADENHAUSEN (*J. pr. Chem.*, 1895, [2], **52**, 433—454).—The method adopted for the preparation of ethylic salts of substituted amido-acids containing an acid radicle consists in warming ethylic amidoacetate hydrochloride with an acid anhydride and anhydrous sodium carbonate, the change occurring in the sense of the equation $2NH_2{\cdot}CH_2{\cdot}COOEt,HCl + (R{\cdot}CO)_2O + Na_2CO_3 = 2R{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOEt + 2NaCl + 2H_2O + CO_2$. An acidic chloride may be substituted for the anhydride, but if the sodium carbonate is omitted, the yield is very small. In this way, ethylic hippurate, ethylic acetylamidoacetate, ethylic succinylamidoacetate, and ethylic phthalylamidoacetate have been prepared, and details of the necessary operations are given. Ethylic succinylamidoacetate was prepared by Haller and Arth, who named it ethylic succinimidoacetate (Abstr., 1887, 1031); the author ascribes to it the formula



$$\begin{array}{l} C_2H_4{\cdot}C{:}N{\cdot}CH_2{\cdot}COOEt \\ \,| \qquad\;\; | \\ CO{-}O \end{array},$$

and a similar constitution to ethylic phthalylamidoacetate.

*Acetamidoacetohydrazide*, $NHAc\cdot CH_2\cdot CO\cdot NH\cdot NH_2$, is prepared by mixing the calculated quantities of ethylic acetamidoacetate and hydrazine hydrate, alcohol and water being eliminated; it forms long, prismatic crystals, melts at 115°, and dissolves fairly easily in alcohol and water, but not in ether. During its preparation some *diacetamidoacetohydrazide*, $(NHAc\cdot CH_2\cdot CO)_2N_2H_2$, is formed, and remains undissolved by alcohol; this compound is a white, crystalline powder, which is somewhat soluble in water, and melts and decomposes at 250°. *Benzylideneacetamidoacetohydrazide*,

$$NHAc\cdot CH_2\cdot CO\cdot NH\cdot N\text{:}CHPh,$$

from acetamidoacetohydrazide and benzaldehyde, crystallises in lustrous laminæ, melts at 198°, and dissolves in alcohol. With nitrous acid, acetamidoacetohydrazide yields a white compound, which probably consists in part of the corresponding azide, but readily breaks up, with elimination of nitrogen and the formation of a compound which is regarded as *acetamidoacetylcarbanil*,

$$NHAc\cdot CH_2\cdot N\text{:}CO;$$

the investigation of this compound is not yet completed.

The reaction between ethylic succinamidoacetate and hydrazine hydrate does not yield the corresponding hydrazide, but a *compound*, $C_8H_{16}N_6O_4$, which forms colourless crystals and dissolves freely in water, but only sparingly in alcohol; it forms a white condensation product with benzaldehyde, and may therefore be supposed to contain the group $(N\cdot NH_2)''$ or $(NH\cdot NH_2)'$.

Ethylic phthalylamidoacetate yields phthalylhydrazide (Abstr., 1895, i, 354) when treated with hydrazine hydrate.

Ethylic phenylamidoacetate and hydrazine hydrate yield *phenylamidoacetohydrazide*, $NHPh\cdot CH_2\cdot CO\cdot NH\cdot NH_2$, which crystallises in large, transparent tables, melts at 126·5°, and dissolves freely in warm alcohol and water, but only sparingly in ether; it reduces Fehling's solution. *Benzylidenephenylamidoacetohydrazide*,

$$NHPh\cdot CH_2\cdot CO\cdot NH\cdot N\text{:}CHPh,$$

crystallises in white needles and melts at 176°. *Isopropylidenephenylamidoacetohydrazide*, $NHPh\cdot CH_2\cdot CO\cdot NH\cdot N\text{:}CMe_2$, crystallises in white needles and melts at 183°.

*Nitrosophenylamidoacetylazoimide*, $NO\cdot NPh\cdot CH_2\cdot CO\cdot N_3$, is formed, together with nitrosodiphenylamine, when phenylamidoacetohydrazide (1 mol.) is treated in the cold with sodium nitrite (2 mols.) and glacial acetic acid; it crystallises in slender, yellow needles, melts at 41—42°, and dissolves in cold alcohol, ether, benzene, and acetone, but not in water.

*Fumarylhydrazide*, $C_2H_2(CO\cdot NH\cdot NH_2)_2$, is prepared from dimethylic fumarate and hydrazine hydrate; it crystallises in lustrous, colourless laminæ, becomes yellow at 200°, melts and decomposes at 220°, and dissolves somewhat freely in hot water, very sparingly in alcohol, and not at all in ether.

*Isopropylidenefumarylhydrazide*, $C_2H_2(CO\cdot NH\cdot N\text{:}CMe_2)_2$, forms white crystals and melts at 220°; when treated with benzaldehyde, it yields the corresponding *benzylidene* derivative, $C_2H_2(CO{\cdot}NH{\cdot}N{:}CHPh)_2$, which crystallises in white laminæ and decomposes at about 220°.

*Fumarylazoimide*, $C_2H_2(CO{\cdot}N_3)_2$, has been prepared in the usual manner as a colourless, crystalline compound, but it explodes when dried. By heating it with absolute alcohol, nitrogen is eliminated, and *ethylic fumarylcarbamate*, $C_2H_2(NH{\cdot}COOEt)_2$, is obtained; this forms small, yellow needles, which become dark when heated, and melt and decompose at 220°; it is a neutral compound, and dissolves freely in water, alcohol, ether, acids, and alkalis. A. G. B.

**Optically Active Halogen Compounds.** By Paul Walden (*Ber.*, 1895, **28**, 2766—2773).—The author replies to Le Bel's criticisms (Abstr., 1895, i, 585) on his previous work (Abstr., 1895, i, 450).

On treating Fileti's *d*-isopropylphenylglycollic acid with phosphorus pentachloride, inactive chlorisopropylphenylacetic acid, melting at 82°, was obtained, but by operating more carefully with *l*-isopropylphenylglycollic acid, a *dextrochlorisopropylphenylacetic acid*, melting at 75—76°, and having the specific rotation $[\alpha]_D = +23{\cdot}3°$ in a 3 per cent. benzene solution, was isolated; evidently the active glycollic acid very readily becomes racemic when the hydroxyl group is exchanged for chlorine.

On brominating asparagine by passing nitric oxide through its dilute sulphuric acid solution containing potassium bromide and bromine, *lævobromosuccinamic acid*, $NH_2{\cdot}CO{\cdot}CH_2{\cdot}CHBr{\cdot}COOH$, is readily obtained; it forms large crystals melting at 146°, and has the specific rotation $[\alpha]_D = -67{\cdot}12°$, $-67{\cdot}57°$, and $-44{\cdot}3°$ in alcohol, ethylic acetate, and 20 per cent. sulphuric acid solutions respectively. When further treated with bromine and nitric oxide in acid or alkali solution, it yields *lævobromosuccinic acid*, which crystallises in striated prisms melting and decomposing at 173°, and has the specific rotations of $[\alpha]_D = -72{\cdot}6°$ to $-72{\cdot}7°$ and $-67{\cdot}92°$ in ethylic acetate and alcohol respectively; it is less soluble in the ordinary reagents than its known racemic isomeride. The *methylic* salt boils at 130° under 22 mm. pressure, and has the rotation $[\alpha]_D = -46°$ in a 50-mm. tube; the dextro-isomeride boils at 126° under 18 mm., and has the rotation $[\alpha]_D = +48{\cdot}3°$ in a 50-mm. tube; the discrepancies are due to the readiness with which these compounds change into inactive methylic fumarate on distillation. The author has repeated and confirmed Piria's and Pasteur's statements respecting the conversion of asparagine and aspartic acid into lævomalic acid, and Tilden and Marshall's observation (Trans., 1895, 494) that asparagine yields lævochlorosuccinic acid when treated with nitrosyl chloride.

Lævoasparagine can therefore be converted into lævobromo- or chloro-succinic acid, and also (Abstr., 1893, i, 250) into the dextrorotatory isomerides of these compounds; the somewhat remarkable result is thus obtained, that by treating an optically active substance containing only one asymmetric carbon atom with inactive reagents at relatively low temperatures, either optical isomeride of the substance formed may be obtained at will. W. J. P.

**Thiosinamine (Allylthiocarbamide) and its Halogen Additive Products.** By J. GADAMER (*Arch. Pharm.*, 1895, **233**, 646—684).—A *substance*, $C_4H_8N_2S,2AgNO_3$, may be obtained by adding excess of a 10 per cent. solution of silver nitrate to a dilute aqueous or alcoholic solution of allylthiocarbamide, acidified with a drop of nitric acid, and is deposited, after a short time, in the form of grey, matted needles. It was obtained in an impure state by Falke (*Diss.*, 1893). When dissolved in water, it decomposes, and the solution subsequently deposits a new *compound*, $C_4H_8N_2S,AgNO_3$, which crystallises from water in long, silky needles. Picric acid displaces one molecular proportion of nitric acid from these compounds, the *substances* formed having the compositions $C_4H_7N_2SAg,C_6H_3N_3O_7,AgNO_3$, and

$$C_4H_7N_2SAg,C_6H_3N_3O_7$$

respectively; they are amorphous, but the former becomes crystalline spontaneously.

A *compound*, $C_4H_8N_2S,HgCl_2$, is obtained by the action of mercurous chloride on an aqueous solution of allylthiocarbamide, or by the action of allylthiocarbamide on the compound $C_4H_6N_2S,2HgCl_2$. It crystallises in large prisms, which have the remarkable property of being half transparent, half opaque.

The interaction of allylthiocarbamide and mercuric cyanide yields the *compounds* $5C_4H_8N_2S,Hg(CN)_2$, forming large, shining crystals resembling those of mercuric cyanide, and $2C_4H_8N_2S,Hg(CN)_2$, which is obtained as grey, microcrystalline aggregates.

Cuprous chloride yields the *compounds* $C_4H_8N_2S,CuCl$, first obtained by Falke (*loc. cit.*), and $(C_4H_8N_2S)_3,Cu_2Cl_2$, which forms small, shining crystals.

When allylthiocarbamide is triturated with mercury, it yields mercuric sulphide and a new *compound*, which is a yellowish mass, soluble in alcohol, and melting at 79—80°. With allylthiocarbamide, copper and silver yield *compounds* of unknown constitution.

*Methylallylthiocarbamide dibromide*, $C_5H_{10}N_2SBr_2$, is formed on mixing alcoholic solutions of methylallylthiocarbamide and bromine. It forms large, white crystals, very soluble in water, and melts at 145—146°; the *picrate* melts at 181—182°. The *chlorobromide*, $C_5H_{10}N_2SBrCl$, obtained from the dibromide by the action of silver chloride, is readily soluble in water, and melts at 120—123°. The *platinochloride* is obtained as large, yellow, nodular aggregates; the *aurochloride* is crystalline, melts at 80°, and dissolves sparingly in water.

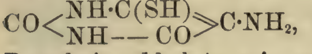
*Dimethylallylthiocarbamide* is obtained on mixing alcoholic allylthiocarbimide and dimethylamine in molecular proportion; it is a liquid, crystallising only at the temperature produced by a mixture of solid carbonic anhydride and ether. The *dibromide*, which crystallises in large, white needles, melting at 207·5—208°, is very soluble in water, dissolving less readily in alcohol; the *chlorobromide* forms large, transparent, colourless crystals, and melts at 191—192°. The *aurochloride* is deposited as a red oil, which gradually becomes crystalline; it melts at 70°. The *platinochloride* is more readily soluble, and crystallises in shining, yellow needles.

Allylthiocarbamide combines with trimethylamine at a temperature of 150—160°, forming an oily liquid. *Trimethylallylthiocarbamide dibromide* is an indistinctly crystalline mass, which is insoluble in alcohol, and yields a pale yellow *platinochloride.*

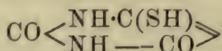
Dimethylallylthiocarbamide unites with silver nitrate, and with cuprous chloride. The *silver compound*, $C_6H_{12}N_2S,AgNO_3$, crystallises in needles, and yields a well crystallised *picrate*. The *copper compound*, $C_6H_{12}N_2S,CuCl$, was obtained in small, brownish crystals. Both compounds yield metallic sulphides when heated with aqueous ammonia. On mixing alcoholic solutions of dimethylallylthiocarbamide and mercuric chloride, a voluminous precipitate is produced.

When triturated with mercury in presence of alcohol, dimethylallylthiocarbamide is attacked, and a stable mercury *compound* is formed, together with mercuric sulphide.

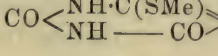
The author regards it as highly probable that dimethylallylthiocarbamide has the constitution $NMe_2{\cdot}C(SH){:}N{\cdot}C_3H_5$. A. L.

**Thio-Compounds of the Uric acid Group.** By EMIL FISCHER and LORENZ ACH (*Annalen*, 1895, **288**, 157—176).—*Thiouramil*,  $CO{<}\begin{matrix}NH{\cdot}C(SH)\\NH{-}{-}CO\end{matrix}{>}C{\cdot}NH_2$, is prepared in the following manner. Potash is added to uric acid (60 grams), suspended in warm water (2,400 c.c.) until a clear solution is obtained; this is diluted with water (1,400 c.c.), treated with a freshly prepared solution of ammonium sulphide (1,000 c.c.), and heated for 5—6 hours at 155—160°. The clear liquid thus obtained, on cooling, deposits the ammonium derivative of thiouramil, and a further quantity of the product is obtained by removing ammonia and ammonium sulphide, and rapidly evaporating the solution, which is then acidified with glacial acetic acid. Thiouramil dissolves in 500—600 parts of boiling water, and separates in minute leaflets or prisms as the liquid cools; it is readily soluble in concentrated sulphuric acid, and is precipitated on diluting the liquid with water. Solutions in cold alkalis rapidly become red when exposed to the air. Cold concentrated nitric acid and the warm dilute acid act on thiouramil, giving rise to sulphuric acid and alloxan; thiouramil gives the murexide reaction, which can also be obtained by the use of chlorine water as the oxidising agent. A fir splinter is at once stained orange when immersed in a neutral or acid solution of thiouramil. Chlorides of the heavy metals yield a white precipitate with an aqueous solution of thiouramil; silver nitrate gives rise to a gelatinous precipitate, which becomes black when heated, or on treatment with ammonia. The *potassium* derivative crystallises in yellowish needles or prisms containing $1H_2O$, which is lost at 130°; the *sodium* derivative also forms yellow needles containing $1H_2O$, which is lost at 105°. The *ammonium* derivative crystallises in lustrous, golden-yellow leaflets, dissolving with difficulty in cold water and ammonium sulphide. When heated with hydrochloric acid for four hours at 150°, thiouramil is converted into a mixture of ammonium chloride and glycocine hydrochloride. *Methylthiouramil*, $C_5N_3H_7SO_2$, is obtained by agitating methylic iodide with a solution of the potassium derivative in water; it crystallises from hot water in stellar aggregates of needles, and darkens at 230° when rapidly heated, melting and decomposing at 252—253° (uncorr.). The neutral solution does not stain fir-wood, but colour is developed in the fibre on adding hydrochloric acid; it gives the murexide reaction when oxidised with chlorine water. The methyl derivative dissolves readily in hot mineral acids, and also in cold alkalis and alkali carbonates; on adding alcohol to the solution in caustic soda, the *sodium* derivative separates in minute, slender needles. Nitric acid oxidises the methyl derivative yielding alloxan, and when the substance is heated with hydrochloric acid for four hours at 150°, carbonic anhydride, ammonia, and methylic mercaptan are produced. *Ethenylthiouramil*, $C_6N_3H_5SO_2$, is obtained by heating the ammonium derivative in a reflux apparatus with acetic anhydride; it dissolves in 210—220 parts of boiling water, from which it separates in needles, melting, when rapidly heated, at 220—221° (uncorr.). The substance dissolves in hot glacial acetic acid, concentrated mineral acids, and hot dilute alkalis, the *sodium* derivative being precipitated in slender needles on adding alcohol to the solution in caustic soda; silver nitrate forms a gelatinous precipitate when treated with the solution in ammonia, and this consists of the *silver* derivative, which crystaliises from hot ammonia in minute, slender prisms. The ethenyl derivative gives the murexide reaction.

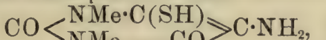
*Azurilic acid*, $C_4H_5N_5O_3$, is obtained by treating an alkaline solution of uric acid with a large excess of ammonium sulphide which has been kept for many months; a mixture of compounds is formed, and after treating this product with dilute nitric acid at 50—60°, azurilic acid is separated in the form of its *silver* derivative. If rapidly heated, the substance becomes coloured at 245°, and decomposes at 275°, when the odour of hydrogen cyanide becomes perceptible. It dissolves in 55 parts of hot water, from which it crystallises on cooling, and is also soluble in alcohol. It is readily soluble in alkalis and alkali carbonates, the solution in caustic soda yielding the *sodium* derivative on adding alcohol; it gives the murexide reaction.

*β-Thiopseudouric acid*,  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C(SH)}\\ \mathrm{NH\text{ —— }CO}\end{matrix}>\mathrm{C\cdot NH\cdot CO\cdot NH_2}$, is obtained by boiling an aqueous solution of potassium cyanate with thiouramil; it crystallises in prisms, and contains $1H_2O$, which is lost at 130°. The acid is soluble in hot water, but dissolves with difficulty in boiling alcohol; alkalis and alkali carbonates dissolve it readily, and when silver nitrate is added to the solution in ammonia, a colourless, gelatinous precipitate is formed, becoming black when heated. Staining of fir-wood is only effected after prolonged boiling, but the murexide reaction is easily produced.

*Oxalyldithiouramil*, $C_2O_2(C_4H_4N_3SO_2)_2$, is obtained by adding the foregoing acid to fused oxalic acid, and heating the clear liquid until the oxalic acid is removed; it is a crystalline powder, dissolving in 400 parts of hot water, and is slowly converted into oxalic acid and thiouramil under the influence of hot, concentrated alkalis.

*β-Methylthiopseudouric acid*,  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C(SMe)}\\ \mathrm{NH\text{ —— }CO}\end{matrix}>\mathrm{C\cdot NH\cdot CO\cdot NH_2}$, is

produced when the methyl derivative of thiouramil is heated on the water bath with an aqueous solution of potassium cyanate; it crystallises from hot water in colourless needles, and when rapidly heated darkens at 290°, and decomposes at 350°. The acid is soluble in 400 parts of hot water, but dissolves with great difficulty in alcohol; in alkalis, it is readily soluble, the metallic derivatives being decomposed by glacial acetic acid, and therefore differing from those of $\beta$-thiopseudouric acid, which are indifferent towards this agent. The acid gives the murexide reaction; the *silver* derivative is soluble in ammonia, and the *potassium* derivative crystallises in pale yellow needles, becoming darker on exposure to air.

*Thiodimethyluramil*,  $CO<\begin{matrix}NMe\cdot C(SH)\\ NMe — CO\end{matrix}>C\cdot NH_2$, is obtained by heating dimethyluric acid, dissolved in ammonia, with freshly prepared ammonium sulphide for two hours at 135—140°; when rapidly heated, it begins to undergo change above 200°, and is completely decomposed about 300°. It dissolves in 70 parts of hot water, and crystallises in colourless needles, which become green in the air; it is readily soluble in hot alcohol, and crystallises in slender prisms. It dissolves readily in alkalis and alkali carbonates, and in other respects resembles thiouramil. M. O. F.

**Hydrazides and Azides (Azoimides) of Carbonic acid.** By Theodor Curtius and Karl Heidenreich (*J. pr. Chem.*, 1895 [2], **52**, 454—489; compare Abstr., 1894, i, 166).—Semicarbazide hydrochloride melts at 175° (Abstr., 1894, i, 165). Carbamic azoimide (carbaminazoimide, Abstr., 1895, i, 252) melts at 97°.

*Carbohydrazide*, previously called carbazide (Abstr., 1894, i, 166), melts at 152°; its *hydrochloride*, $CO(NH\cdot NH_2)_2,2HCl$, melts at 210°, and its *sulphate* melts and decomposes at 218°. A *diacetyl derivative* was prepared.

Carbazoimide has already been described as carbonyl nitride (Abstr., 1895, i, 12); attention is called to the analogy of its reactions to those of carbonyl chloride. The *silver derivative* of methenylcarbohydrazide, $C_2H_3N_4OAg$, is a white powder, stable in light.

*Methylic azoimidocarbonate*, $N_3\cdot CO_2\cdot Me$, is prepared by treating ammonium azoimide with methylic chlorocarbonate in ethereal solution. It is a colourless liquid, and boils at 102°, but is liable to explode at this temperature.

The hydrazine salt of dicarbamide (*loc. cit.*) melts at 197°; the *silver* salt, $C_2H_3N_4O_2Ag$, is a white powder stable in light.

*Hydrazine thiocyanate*, $N_2H_5SCN$, is prepared by decomposing hydrazine sulphate with barium thiocyanate; it crystallises in tablets, melts at 80°, and dissolves freely in water and alcohol. When heated in a sealed tube at 100° for 4—5 hours, it yields *hydrazidothiocarbonamide*, $NH_2\cdot CS\cdot NH\cdot NH\cdot CS\cdot NH_2$, which crystallises from hot water in long, colourless prisms, and melts at 214—215°; one part dissolves in 418·5 parts of water at 23°.

The remainder of the compounds described in this paper have already received notice in the places quoted. A. G. B.

**A Derivative of Furfuraldehyde from Lævulose.** By JOSEPH KIERMAYER (*Chem. Zeit.*, 1895, **19**, 1003—1005; compare Düll, this vol., i, 121).—The product obtained by Düll, by the action of oxalic acid on lævulose is shown by the author to be a derivative of furfuraldehyde. It is most readily prepared from cane sugar, as the glucose produced by inversion is not acted on. A 30 per cent. aqueous solution of cane sugar is heated with 0·3 per cent. oxalic acid for 3 hours under a pressure of three atmospheres; the mixture is neutralised with calcium carbonate, treated with basic lead acetate, and then extracted with ether or ethylic acetate. The aldehyde forms a colourless syrup, which rapidly turns yellow on exposure to the air. It is readily soluble in water, alcohol, and ethylic acetate, more sparingly in ether. It begins to boil and froth at 60°, but even when the temperature has reached 200° only a slight distillate is obtained, and this consists of furfuraldehyde; on further heating, however, it is completely decomposed, and cannot be distilled even under diminished pressure. Its alcoholic solution gives a deep scarlet coloration with thymol and sulphuric acid, and a deep red with phloroglucinol. Both are extremely delicate reactions. It acts as a strong reducing agent towards ammoniacal silver nitrate and Fehling's solution. The author considers it is probably *β-hydroxy-δ-methylfurfuraldehyde*, $OH\cdot C_4OHMe\cdot COH$. The *phenylhydrazone* forms golden-yellow crystals and melts at 138°, the *anti-aldoxime* melts at 77—78°, and if allowed to remain for some time in alkaline solution is converted into the *syn-aldoxime*, which melts at 108°. The syn-aldoxime is converted back again into the anti-compound when heated for 30 mins. at 115—120°. The author shows that a similar treatment converts furfur-*syn*-aldoxime into furfur-*anti*-aldoxime.

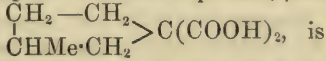
When the aldehyde is oxidised by ammoniacal silver nitrate, it yields *β-hydroxy-δ-methylpyromucic acid*, $OH\cdot C_4OHMe\cdot COOH$; this is readily soluble in water, sparingly in ether, melts at 148°, and at the same time undergoes decomposition. Its solution is coloured yellow by ferric chloride. The *silver salt* crystallises with $1H_2O$ in colourless prisms, it is sparingly soluble in water, and readily blackens on exposure to light. The *copper* and *calcium* salts are also described. The *benzoyl derivative*, $C_6H_5O_3\cdot COPh$, crystallises in long needles, melts at 55° and is readily soluble in ethylic acetate, benzene, and alcohol.

When the aldehyde is heated with oxalic acid and water under a pressure of three atmospheres, it is converted into levulinic acid. Reasons for considering the aldehyde as a β-hydroxy-compound are given.

When the pure aldehyde is allowed to remain over sulphuric acid, in the course of a few days it loses water and forms *methylfurfuraldehyde oxide*, $O(C_4OHMe\cdot COH)_2$; this oxide is also obtained by the distillation of the aldehyde. It crystallises in long feathery needles, melts at 112°, is sparingly soluble in hot water and in ether, and insoluble in benzene and acetic acid. The aqueous solution readily reduces ammoniacal silver nitrate and Fehling's solution, and gives colorations with phenols. The *anilide*, $(C_6H_5O\colon NPh)_2O$, forms colourless plates and melts at 124°, the *phenylhydrazone*,

$(C_6H_5O{:}N{\cdot}NHPh)_2O$, melts at 139°, and the *syn-aldoxime* at 167—168°. This oxime is soluble in ethylic acetate and acetone, only sparingly in chloroform, ether, and benzene, and more readily in hot dilute alcohol than in concentrated.

Sorbinose, when heated with aqueous oxalic acid, also yields the same methylhydroxyfurfuraldehyde. Dextrose, on the other hand, is not acted on by a 0·5 per cent. solution of oxalic acid, lactose behaves similarly. J. J. S.

**Synthesis of β-Methylpentamethylenecarboxylic acids.** By Wilhelm Euler (*Ber.*, 1895, 2952—2959).—Pyrotartaric nitrile, $CN{\cdot}CHMe{\cdot}CH_2{\cdot}CN$ (Claus, *Annalen*, **191**, 33), is obtained by heating allylic iodide with potassium cyanide in alcoholic solution and fractionating the product; it boils at 240—260°, or at 130—140° under 20 mm. pressure, but the yield of it is only 5 per cent. of the weight of the allylic iodide, the chief product of the reaction being β-ethoxybutyronitrile. By reducing it with sodium in alcoholic solution it is converted into the diamine (Oldach, Abstr., 1887, 735), the *dihydrochloride* of which melts at 144—145°. When this salt is decomposed, in ice-cold solution, with the equivalent quantity of silver nitrite, and the filtered solution slowly distilled until the temperature reaches 140°, *β-methyltetramethylene glycol*, $OH{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ is obtained, together with an oil boiling between 70° and 130°; the latter is probably a mixture of the unsaturated alcohols, $OH{\cdot}CH_2{\cdot}CHMe{\cdot}CH{:}CH_2$ and $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, as it forms a *dibromo-additive compound*, and also a *monacetate* boiling at 120—130°; a hydrocarbon, $CH_2{:}CMe{\cdot}CH{:}CH_2$, is probably formed in addition. The glycol boils at 115—130° under 20 mm. pressure; when it is saturated with hydrogen bromide at 0° and then heated at 110°, it yields *β-methyltetramethylene dibromide*. If this is heated with ethylic disodiomalonate in alcoholic solution, and the fraction of the product that boils above 135° under 18 mm. pressure is hydrolysed with 10 per cent. aqueous alcoholic potash, *β-methylpentamethylenedicarboxylic acid*,  $\begin{array}{l}CH_2{-}CH_2\\ \vert\\ CHMe{\cdot}CH_2\end{array}\!\!>C(COOH)_2$, is obtained. This melts at 140—142°, and then loses carbonic anhydride, the *monocarboxylic acid* finally distilling over at about 220°. Of the latter only a few drops were obtained, although 8 kilos. of allylic iodide were worked up; its *calcium salt*, with $5H_2O$, and the *silver salt* were, however, prepared and analysed. C. F. B.

**New treatment of the Benzene Problem: Derivatives of Thymotic acid.** By Georg Heyl and Victor Meyer (*Ber.*, 1895, **28**, 2776—2798).—In order to obtain some insight into the constitution of the benzoic acids, and, therefore, of the aromatic compounds, the etherification of certain fatty acids has been studied on the same lines as that of the substituted benzoic acids. Acids such as aconitic acid,

$$COOH{\cdot}CH_2{\cdot}C(COOH){:}CH{\cdot}COOH,$$

and tricarballylic acid, $COOH\cdot CH_2\cdot CH(COOH)\cdot CH_2\cdot COOH$, readily yield tri-ethereal salts when treated with alcohol and hydrogen chloride at 0°, whilst the corresponding aromatic acid, hemimellitic acid, does not yield a tri-salt under these circumstances. This shows that the reaction characteristic of aromatic acids does not hold with others containing the same groups, since the three carboxyl groups of their acids are adjacent.

The aromatic acids may be supposed to contain either the group $COOH\cdot C{<}^{C}_{C}$ or $COOH\cdot C\begin{array}{l}/C\\ -C,\\ \backslash C\end{array}$ according to the benzene formula which is accepted. The authors, therefore, next studied the etherification of certain fatty acids which also contain these groups. Triphenylacrylic acid, $COOH\cdot C{<}^{CPh_2}_{Ph}$, contains the first whilst the second is present in triphenylacetic acid, $COOH\cdot CPh_3$. The essential point is, that the group COOH·C is connected with *tertiary* carbon atoms; the phenyl group is chosen simply because the carbon atom which is directly combined with the group COOH·C is a tertiary one. Neither of these acids is completely etherified by alcoholic hydrogen chloride in the cold, triphenylacrylic acid yielding 22·3 per cent., and triphenylacetic acid only 3·45 per cent. of ethereal salt. When treated with hydrogen chloride in boiling alcoholic solution, the triphenylacrylic acid gives 97 per cent. of ethereal salt, whilst triphenylacetic acid only gives 22·3 per cent.; the behaviour of triphenylacetic acid is therefore precisely analogous to that of a diorthosubstituted benzoic acid. It follows that substances which contain the group $COOH\cdot C\begin{array}{l}/C\\ -C\\ \backslash C\end{array}$ behave, in this respect, as aromatic substances, whilst those which contain the group $COOH\cdot C{<}^{C}_{C}$ do not.

Triphenylacrylic acid may be prepared from benzophenone chloride and benzylic cyanide, as already described (Abstr., 1895, i, 542), or by heating benzophenone chloride with methylic phenylacetate. In this case, it is accompanied by a small amount of *diphenylindone*, which forms dark orange-red crystals, and melts at 150—151°. Triphenylpropionic acid is readily etherified by boiling alcoholic hydrogen chloride, so that the characteristic behaviour of triphenylacetic acid is not merely due to the presence of three phenyl groups.

The authors have also endeavoured to resolve nitrothymotic acid, $NO_2\cdot C_6HMePr(OH)\cdot COOH$, and formylthymotic acid,

$$CHO\cdot C_6HMePr(OH)\cdot COOH,$$

which contain six different groups, into optically active constituents, but without success. Similar experiments with metahydroxybenzoic acid also gave a negative result.

*Nitrothymotic* acid is obtained by the direct nitration of thymotic acid, and crystallises in yellowish plates, melting at 173—175°.

*Formylthymotic acid* is prepared by heating thymotic acid with chloroform and aqueous soda. It melts at 180—185°. A. H.

**The Benzene Problem.** By JULIUS W. BRÜHL (*Ber.*, 1895, **28**, 2981—2986).—The author thinks that no definite conclusions respecting the structure of the benzene ring can be drawn from the work of Heyl and V. Meyer (preceding abstract). By means of figures, it is shown, that from stereochemical considerations triphenylacetic acid would probably be difficult to etherify. J. J. S.

**Action of Nascent Bromine on Benzene Derivatives.** By WILHELM VAUBEL (*J. pr. Chem.*, 1895, [2], **52**, 417—423; compare Abstr., 1894, i, 94, 453).—Amido- and hydroxy-derivatives, be they primary, alkylised or acetylised, when united directly to the nucleus, possess, beyond all other substituents, the property of facilitating the entrance of bromine in place of nucleal hydrogen. The bromine always takes the ortho- and para-positions with regard to the $NH_2$- and OH-groups. None of the usual substituents—such as $CH_3$, $NO_2$, halogen, $SO_3H$, COOH, N:NR, N:NCl—prevents the entrance of bromine, should the substituent itself occupy the ortho- or para-position to $NH_2$ or OH. Exceptions are $NH_2$ and OH themselves; these in the ortho- or para-position to each other hinder bromination, and the action of bromine effects oxidation.

The carboxyl and sulphonic groups are displaced by bromine when they are in the ortho- or para-position to an amido- or hydroxy-group. This tendency remains when another substituent (for example, $CH_3$ or $NO_2$), is in the meta-position with respect to the said groups. An $SO_3H$ or COOH group in the meta-position relatively to $NH_2$ or OH is not displaced by bromine.

Alkylised or acetylised OH and $NH_2$ groups exert a smaller orientating influence on bromine. The dialkylised amido-group shows this to a greater extent than the monalkylised group. A. G. B.

**Note (Synthesis of Aromatic Hydrocarbons).** By PAUL JANNASCH (*Ber.*, 1895, **28**, 2823).—In order to avoid clashing with Töhl (this vol., i, 16), the author points out the direction in which he is pursuing his researches on the substituted benzenes.

A. H.

**Symmetrical Trinitrobenzene.** By CORNELIUS A. LOBRY DE BRUYN and FREDERIK H. VAN LEENT (*Rec. Trav. Chim.*, 1895, **14**, 150—155; compare Abstr., 1895, i, 574).—When the calculated quantity (1 mol.) of a very concentrated solution of potassium hydroxide is added to a solution of symmetrical trinitrobenzene in 96 per cent. methylic alcohol, red crystals of a substance are deposited after a time, whilst dinitroanisoïl remains dissolved in the mother liquor. The new substance has the composition represented by the formula $[C_6H_3(NO_3)_3,MeOK]_2 + H_2O$. If heated on platinum foil, it detonates violently, and, when treated with dilute acids, symmetrical trinitrobenzene is regenerated. When sodium hydroxide was used instead of potassium hydroxide, no analogous crystalline derivative could be isolated, although the solution became red. If ethylic alcohol is substituted for methylic alcohol, the reducing action of the former is so great that brown, amorphous compounds are alone produced. A. R. L.

**Phenylnitromethane (exo-Nitrotoluene).** By Arnold F. Holleman (*Rec. Trav. Chim.*, 1895, **14**, 121—130).—The observations on the boiling point of phenylnitromethane (phenylnitromethane, Abstr., 1895, i, 455) have been confirmed by Gabriel in a communication to the author, who has prepared phenylnitromethane by the method previously described by himself (*loc. cit.*), and also by Gabriel's method (Abstr., 1884, 902). The products had the same boiling point in both cases, and gave a benzenazo-derivative melting at 101°.

The action of one equivalent of bromine on exo-nitrotoluene furnishes a mixed product. Exo-nitrotoluene dissolves in concentrated sulphuric acid, but the product soon resinifies.

*Exometadinitrotoluene*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NO_2$, is obtained when phenylnitromethane is dropped into cooled nitric acid of sp. gr. 1·5 (7 parts), care being taken that the temperature does not exceed 10° during the reaction. The new compound is colourless, melts at 94°, and is soluble in the usual solvents, but crystallises best from glacial acetic acid. Its constitution is proved by the fact that it yields metanitrobenzoic acid on treatment with alkaline permanganate. The *sodium* and *potassium* derivatives are red, and crystallise in needles; their solutions are faintly alkaline towards litmus, and are decolorised on addition of an acid, yielding the parent compound. Inasmuch, however, as exometadinitrotoluene is a strong acid it cannot be used as an indicator. The solutions of the alkali salts give, with silver nitrate, a gelatinous precipitate, which blackens on being heated; with copper sulphate (heated), blue triclinic crystals; with lead acetate, a yellowish-white precipitate, and with mercuric chloride a white, amorphous precipitate.

An *additive compound*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NO_2, NH_3, H_2O$, separates in yellow, silky needles, when an alcoholic solution of exometadinitrotoluene is treated with alcoholic ammonia, ether being subsequently added. It dissociates very readily, becoming white on exposure to the air for a single day.

From the mother liquor obtained in the preparation of exometadinitrotoluene, an isomeric substance was isolated, which also was found to yield metanitrobenzoic acid on oxidation; the specimen analysed melted between 65° and 80°. The colour of the alkali salts of this substance is yellow, and is only slowly discharged when a solution is treated with an equivalent of acid, exometadinitrotoluene then separating. The phenomenon can be explained by assuming that the yellow anions are transformed into colourless tautomeric anions. Determinations of the molecular conductivity of the solution during its change of colour, which diminishes in proportion as the colour vanishes, lead to the same conclusion.

It seems probable, therefore, that exometadinitrotoluene exists in two modifications, one of which—that forming yellow salts—contains the group NOH. A. R. L.

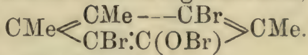
**Ozotoluene.** By ADOLPHE RENARD (*Compt. rend.*, 1895, **121**, 651—652).—The action of ozone on commercial toluene yields a black, tarry, acid, non-explosive product, but if after the action of the ozone has continued from 10 to 12 hours, the toluene is separated, washed with alkali, redistilled, and again heated with ozone at 0°, it yields *ozotoluene*, $C_7H_8O_6$, a white, translucent, gelatinous substance, which becomes white and opaque if the toluene is evaporated in a current of air. In dry air, it begins to decompose at 8° or 10°, and in moist air it is decomposed at once. It detonates when heated or struck, but less readily than ozobenzene (Abstr., 1895, i, 593). In contact with concentrated aqueous potash, it decrepitates briskly, but, unlike ozobenzene, it does not explode in contact with ammonia or concentrated sulphuric acid. Water decomposes it with development of heat and formation of formic and benzoic acids, a result which shows that the benzene nucleus remains intact.

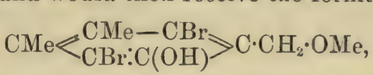
Pure orthoxylene, when treated with ozone at 0°, likewise yields a white explosive compound, similar to ozobenzene and ozotoluene.

C. H. B.

**Conversion of Nitriles into Amides by Hydrogen Peroxide.** By J. DEINERT (*J. pr. Chem.*, 1895, [2], **52**, 431—432).—The author has applied Radziszewski's method (Abstr., 1885, 496) to sundry nitriles, and has obtained fair yields of the corresponding amides from benzonitrile, benzylic cyanide (in alkaline solution), paratoluonitrile, and β-naphthonitrile. Propionitrile and α-naphthonitrile gave very poor yields, whilst orthotoluonitrile was not converted at all.

A. G. B.

**An Abnormal Tribromo-derivative of Pseudocumenol.** By KARL AUWERS (*Ber.*, 1895, **28**, 2888—2902; compare the two following abstracts).—The remarkable reactions of the tribromo-derivative of pseudocumenol, which are described in the two following abstracts, seem to be best explained by the formula  $\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{-}{-}{-}CBr}\\ \mathrm{CBr{:}C(OBr)}\end{matrix}{>}\mathrm{CMe}$. The methoxy-compound would then receive the formula



$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{-}CBr}\\ \mathrm{CBr{:}C(OH)}\end{matrix}{>}\mathrm{C{\cdot}CH_2{\cdot}OMe},$$

the methoxy-group having, by molecular change, been substituted for an atom of hydrogen of the methyl group, whilst this atom of hydrogen goes to form the hydroxyl group, which these derivatives undoubtedly contain. The formulæ of the remaining derivatives are given along with their special description.

A. H.

**An Abnormal Tribromo-derivative of Pseudocumenol.** By KARL AUWERS and J. MARWEDEL (*Ber.*, 1895, **28**, 2902—2910; compare foregoing abstract).—Pseudocumenol yields two bromo-derivatives which contain the bromine atoms in the nucleus (Reuter, *Ber.*, **11**, 29). In addition to these, a third compound can be obtained by treating the phenol with bromine and acetic acid. This substance, *dibromopseudocumenol bromide*, $C_6Me_3Br_2{\cdot}OBr$, crystallises in large, flat needles, and melts at 125—126°. It does not dissolve immediately in alkalis, but is decomposed by them after a time. The bromine atom very readily enters into reaction, and the substance produced is decomposed by alcohols if left in contact with them; by silver nitrate, with formation of silver bromide; and by potassium iodide, iodine being liberated. *Dibromomethoxypseudocumenol*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot OMe$, is obtained by boiling the tribromo-derivative with methylic alcohol. It crystallises in matted, silky needles, melts at 91—92°, and is readily soluble in alkalis, forming solutions from which it is reprecipitated by acids, even after boiling. This substance contains a hydroxyl group, and yields a *benzoate* which crystallises in fascicular groups of silky needles melting at 120°. *Ethoxydibromopseudocumenol* closely resembles the methoxy-compound, and crystallises in silky needles melting at 85—87°. The *benzoate* also forms needles, and melts at 109—110°. The tribromo-derivative also reacts with aniline to form a *compound* of the formula $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot NHPh$, which crystallises in rhomboid forms, and melts at 134—134·5°. This substance forms salts both with alkalis and acids; the *sodium salt* crystallises in silky needles, which are very readily soluble in water, and are decomposed by carbonic anhydride. The salts with acids are crystalline, and almost insoluble in cold water, scarcely soluble in hot water; the *bromide* melts at about 200°, the *chloride* at about 205°, the *nitrate* with decomposition at about 172°, and the *sulphate* indefinitely from 135—150°; the *acetate*, which crystallises in prisms having an adamantine lustre, melts at 223—225°. The *piperidine compound* from the tribromo-derivative forms concentric groups of slender, white needles melting at 91°; it resembles the aniline derivative, but its salts with acids are somewhat more readily soluble in water. The *bromide* melts at 207—208°; the *benzoate* crystallises in small needles melting at 136·5—137·5°. When it is heated on the water bath, piperidine is given off, whilst *tetrabromodihydroxytetramethylstilbene*, $C_2H_2(C_6Me_2Br_2\cdot OH)_2$, remains; this crystallises in matted needles, melts at 232·5—234°, is readily soluble in alkalis without decomposition, but only very sparingly in the ordinary solvents. The *ethyl ether* forms lustrous plates, and melts at 171—172·5°; its molecular weight, determined by the cryoscopic method, agrees with the formula $C_{22}H_{24}Br_4O_2$. A. H.

**An Abnormal Tribromo-derivative of Pseudocumenol.** By KARL AUWERS and S. AVERY (*Ber.*, 1895, **28**, 2910—2923; compare the foregoing abstracts).—When the tribromo-derivative of pseudocumenol is brought into contact with dimethylaniline, the *bromide* of the dimethylaniline derivative separates in the form of leaf-like crystals melting at 234—236°. The free *base*, $OH\cdot C_6Me_2Br_2\cdot CH\colon NMe_2Ph$, crystallises in transparent needles melting at 124°, and resembles the aniline compound in its general properties. The *hydrochloride* crystallises in nacreous plates melting at 216—220°; the *nitrate* melts at 200°, and the *sulphate* at 86—90°; all these salts are insoluble in water, and are decomposed by boiling water. The *benzoate* melts at 156—158°. The presence of the hydroxyl group in this compound is further shown by the fact that it unites with phenylcarbimide to form a *phenylurethane derivative*,

$$NHPh\cdot COO\cdot C_6Me_2Br_2\cdot CH\colon NMe_2Ph,$$

which melts at 186—189°.

When the tribromo-derivative is treated with pyridine, the *hydrobromide* of a *pyridine derivative*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot C_5NH_5Br$, is formed; this is insoluble in water, melts at 234—236°, and crystallises with $1H_2O$ from an acetic acid solution of hydrogen bromide. When it is treated with alkalis, the corresponding base is not liberated, but a *yellow substance*, which is very unstable, is produced; this has the formula $C_9H_8Br_2O\cdot C_5NH_5 + 2H_2O$, and, when heated with aqueous alkalis, yields tetrabromodihydroxytetramethylstilbene, identical with that obtained by heating the piperidine derivitive on the water bath (compare the foregoing abstract). When the yellow compound, however, is heated alone on the water bath or boiled with water, it yields *dibromohydroxypseudocumenol*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot OH$. The same substance can be more conveniently prepared by boiling the tribromo-derivative itself with aqueous acetic acid or aqueous acetone. It crystallises from benzene in lustrous white needles, and melts at 166°; it unites with some difficulty with phenylcarbimide, forming a *compound*, $C_9H_9Br_2O\cdot O\cdot CO\cdot NHPh$, which is a white, crystalline powder melting at 135°. Potassium ferricyanide oxidises the hydroxy-derivative, forming an insoluble substance which has the formula $(C_9H_6Br_2O)_x$, and melts at 200—205°; the constitution of this product has not yet been ascertained. The *ether of dibromohydroxypseudocumenol*, $(OH\cdot C_6Me_2Br_2\cdot CH_2)_2O$, is formed when the hydroxy-compound is boiled with acetic acid and, indirectly, when the tribromo-derivative is dissolved in acetic acid, water added to the hot solution, and the whole boiled. It crystallises in slender, silky needles, and melts at 252°; it is readily soluble without decomposition in aqueous alkalis, and yields a *diacetate*, which melts at 216°. The *acetate* of *dibromohydroxypseudocumenol* is formed along with the ether when the tribromo-derivative is heated with aqueous acetic acid, and may also be prepared by boiling the same substance with glacial acetic acid and sodium acetate, and by treating the hydroxy-compound with acetic anhydride. It is insoluble in water, readily soluble in other solvents, and melts indefinitely at about 113°. When boiled with aqueous acetone, it yields dibromohydroxypseudocumenol. When it is shaken, or ground up with dilute aqueous soda, on the other hand, it yields tetrabromodihydroxytetramethylstilbene (compare foregoing abstract). The tribromo-derivative is reduced by zinc and glacial acetic acid, with formation of dibromopseudocumenol and the acetate of hydroxydibromopseudocumenol, accompanied by a small amount of a substance melting at 270—272°, the constitution of which has not been ascertained. A. H.

**Derivatives of Benzoylcarbinol and of Diphenacyl.** By Victor Fritz (*Ber.*, 1895, **28**, 3028—3034; compare Hunaeus and Zincke, Abstr., 1878, 223; E. Fischer, *Ber.*, **20**, 822; **26**, 2400; Abstr., 1895, i, 440).—Benzoylmethylic phenylic ether, $CH_2Bz\cdot OPh$ (Möhlau, Abstr., 1883, 332), does not reduce Fehling's solution, and is not decomposed at 100° by aqueous alcohol containing 5 per cent.

of hydrogen chloride. The *oxime* crystallises in small, colourless prisms, melts at 113—114° (uncorr.), and is readily soluble in alcohol, ether, benzene, and alkalis. The *phenylhydrazone* is readily soluble in ether and benzene, more sparingly in cold alcohol; it melts at 85—87°, and readily turns brown on exposure to the air.

*Benzoylmethylic β-naphthylic ether*, $CH_2Bz\cdot O\cdot C_{10}H_7$, obtained by the action of bromacetophenone on the sodium derivative of β-naphthol, crystallises in small, colourless needles, and melts at 104—106° (uncorr.). Towards Fehling's solution and hydrochloric acid, it behaves in exactly the same way as the phenylic ether. The *oxime* melts at 144—145°. *Bisethylbenzoylcarbinol* was prepared by the ethylation of benzoyl carbinol (Fischer, Abstr., 1895, i, 440); it crystallises in colourless prisms, melts at 190—192°, and is readily soluble in hot alcohol or ether.

*Bromodiphenacyl*, $COPh\cdot CHBr\cdot CH_2\cdot COPh$, is obtained by the action of sodium and alcohol on an ice-cold solution of bromacetophenone in alcohol; it crystallises in small, colourless, glistening needles, melts at 161—162°, and is only sparingly soluble in alcohol and ether. When treated with alcohol and zinc dust, it yields diphenacyl (Kapf and Paal, Abstr., 1889, 147; Nötling and Kohn, Abstr., 1886, 349; Claus and Werner, Abstr., 1887, 827), and with alcohol and sodium amalgam yields a compound $C_{16}H_{18}O_2$. This crystallises in colourless needles, melts at 93—94°, is readily soluble in alcohol, ether, and benzene, and sublimes when heated above its melting point. It may also be obtained by the reduction of diphenacyl itself with sodium amalgam, and is probably *diphenyltetramethyleneglycol*, $C_2H_4(CHPh\cdot OH)_2$. J. J. S.

**New Salts of Guaiacol.** By H. Dubois (*Chem. Centr.*, 1895, i, 209; from *Apoth. Zeit.*, **9**, 952).—*Guaiacol succinate*,

$$C_4H_4O_4(C_6H_4\cdot OMe)_2,$$

crystallises in fine, silky needles, melts at 136°, is insoluble in water, sparingly soluble in alcohol or ether, but readily in chloroform, acetone, or hot light petroleum. Bromine readily forms substitution products. It is best prepared by dissolving guaiacol in slight excess of sodium hydroxide solution, cooling to 0°, and then adding the requisite quantity of succinic chloride while keeping well stirred. *Guaiacol phosphate*, $PO(O\cdot C_6H_4\cdot OMe)_3$, crystallises in hard, colourless plates, melts at 98°, is readily soluble in chloroform and acetone, but insoluble in water, ether, and light petroleum. It is readily hydrolysed by aqueous potash at 150°, and may be distilled under diminished pressure without decomposing. J. J. S.

**Triresorcinol.** By Oswald Hesse (*Annalen*, 1895, **289**, 61—70).—The *hydrochloride* of triresorcinol, $C_{18}H_{14}O_4,HCl$, is obtained by heating resorcinol (4 grams) with glacial acetic acid (4—6 c.c.) and fuming hydrochloric acid (4 c.c.) in sealed tubes at 85° for 72 hours; it contains $1H_2O$, which is removed at 120°, and crystallises in small prisms which have a fire-red reflex and appear yellow by transmitted light. It is almost insoluble in organic solvents, but dissolves readily in alkalis and alkali carbonates, forming yellowish-red solutions which, on dilution, exhibit intense, green fluorescence. *Triresorcinol*, $OH{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}OH$, obtained by prolonged treatment of the hydrochloride with boiling water, crystallises in short prisms which contain $2\frac{1}{2}H_2O$, and have a dark, bluish-red reflex, appearing yellow by transmitted light; it becomes anhydrous at 120°, and decomposes above 130° without previously melting. Although the substance dissolves sparingly in common solvents, the solutions exhibit intense green fluorescence; it dissolves in alkalis and alkali carbonates, cotton, wool, and silk being dyed yellow by these solutions. The *hydrobromide*, $(C_{18}H_{14}O_4)_4,5HBr$, is obtained by treating the solution in glacial acetic acid with concentrated hydrobromic acid; it is anhydrous, and, although scarcely soluble in cold water, it imparts an intense green fluorescence to this medium. The *diacetyl* derivative crystallises in brownish-red leaflets which melt and decompose at 260—270°.

*Bromotriresorcinol hydrobromide*, $C_{18}H_{13}BrO_4,HBr$, is obtained by adding bromine to a solution of triresorcinol in hot acetic acid and immediately removing the crystals which separate; it contains $1H_2O$, and is decomposed by boiling water, yielding *bromotriresorcinol*, which dissolves readily in boiling water, and exhibits an intense green fluorescence in solution. If excess of bromine is employed, the substance is redissolved, and a *compound* is formed having the composition $(C_{18}H_{10}Br_4O_4)_2,5HBr$; this is readily soluble in boiling water, yielding an intense bluish-violet solution, whilst alkalis and ammonia develop a purple-violet coloration. *Tetrabromotriresorcinol*, $C_{18}H_{10}Br_4O_4$, is obtained by dissolving the foregoing compound in aqueous sodium hydrogen carbonate and treating the liquid with nitric acid; it is insoluble in cold water, and only sparingly soluble in the boiling liquid, yielding a bluish-violet solution. After removing the two products already mentioned, as obtained on brominating triresorcinol, the liquid contains *heptabromotriresorcinol*, $C_{18}H_7Br_7O_4$, a carmine-red compound having a bluish reflex; it contains $2\frac{1}{2}H_2O$, and is insoluble in water, dissolving readily, however, in organic solvents. Alkalis, alkali carbonates, and ammonia give rise to bluish-violet solutions which dye wool, cotton, and silk the same shade.

Barth and Weidel (Abstr., 1878, 61) have obtained diresorcinol and tetraresorcinol by the action of concentrated hydrochloric acid on resorcinol, and the formation of resacetophenone and resaceteïn or acetofluoresceïn under the influence of glacial acetic acid, has been also recorded. M. O. F.

**Action of Potassium Hydroxide and Ethoxide on Quinone.** By CHARLES ASTRE (*Compt. rend.*, 1895, **121**, 530—532).—When potassium ethoxide is added to a dilute solution of quinone in ether, a green compound, $C_6H_3KO_2 + EtOH$, is precipitated. It is stable in dry air or dry oxygen, but rapidly alters in moist air.

The action of concentrated alcoholic potash on quinone develops a large quantity of heat. With a very dilute alcoholic solution of quinone, a mixture of a blue and a yellowish-brown compound is obtained. The careful addition of alcoholic potash to a very dilute ethereal solution of quinone in an atmosphere of hydrogen yields a crystalline blue precipitate of the composition $C_6H_3KO_2+H_2O$. It alters rapidly in presence of moist air or oxygen, or in contact with water or alcohol.

Attempts to obtain a dipotassium derivative of quinone were not completely successful, and the compound seems to be very unstable. A product with a composition corresponding with a compound of one molecule of dipotassium quinone with two molecules of alcohol is obtained on adding a large quantity of ether to a mixture of an alcoholic solution of quinone with excess of alcoholic potash.

C. H. B.

**Peroxidised Potassium Derivatives of Quinone.** By CHARLES ASTRE (*Compt. rend.*, 1895, **121**, 559—561; compare this vol., i, 18).—*Peroxidised dipotassium quinone*, $C_6K_2O_6$, a blackish, crystalline, very hygroscopic compound, is obtained by mixing alcoholic solutions of quinone and potassium hydroxide, heating the mixture at 70—75°, and passing a current of dry oxygen through it for eight to ten hours; it is very soluble in, and is decomposed by, water. The same product is obtained even in presence of a large excess of the alkali. *Peroxidised potassium quinone*, $C_6KHO_6$, is a black compound obtained by dissolving the preceding compound in water and adding sufficient alcohol to bring the alcoholic strength of the mixture up to about 70°, or by passing oxygen through a solution of quinone in a dilute aqueous solution of slightly more than the calculated quantity of potash, and afterwards adding the alcohol.

If quinol is dissolved in alcohol containing three molecular proportions of potassium hydroxide, and treated with oxygen at 70—75°, it likewise yields the compound $C_6K_2O_6$.

The aqueous solutions of these potassium derivatives, when mixed with an acid, yield a black precipitate which is under investigation.

These results indicate that only two of the hydrogen atoms in quinone can be displaced by a metal, and hence afford further evidence of the diketonic character of quinone. C. H. B.

**Action of Sodium Alkyloxides on Chloranil. Acetals derived from Substituted Quinones.** By C. LORING JACKSON and H. S. GRINDLEY (*Amer. Chem. J.*, 1895, **17**, 633—658; compare this vol., i, 19).—*Dichlorodiethoxyquinone tetrethylacetal*, $C_6Cl_2(OEt)_6$, is formed in small quantity by the action of ethylic iodide on silver dichlorodiethoxyquinone hemiacetal; after the dichlorodiethoxyquinone has been removed by treatment with dilute alcoholic soda, the acetal crystallises from light petroleum in large white, rhombic prisms or quadratic plates: it melts at 101—102°, and sublimes at 260—275° without decomposing. When heated with sulphuric acid (sp. gr. = 1·44), it is hydrolysed, dichlorodiethoxyquinone and, in small quantity, chloranilic acid being formed. More dilute acid, alkali, either aqueous or alcoholic, and bromine are without action on the acetal. *Dichlorodiethoxyquinone dibenzoyldiethylacetal*, $C_6Cl_2(OEt)_4(OBz)_2$, is obtained by the action of benzoic chloride on the sodium salt of the hemiacetal suspended in alcohol; it is not formed in presence of ether, nor by the action of benzoic chloride alone at 100° on either the hemiacetal or the sodium salt. The yield is about 66 per cent. of the theoretical. The compound crystallises in short, thick, colourless prisms, melts at 170°, does not react with soda, hydroxylamine, or zinc dust and glacial acetic acid.

Hydroxylamine hydrochloride and dichlorodiethoxyquinone readily combine, forming a black crystalline compound. When the above acetal is heated with sulphuric acid (sp. gr. = 1·44), a compound is formed which is probably the *oxide* of *dichlorodiethoxyquinone dibenzoate*, $C_6Cl_2O(OEt)_2(OBz)_2$, or that of *dichloroquinone benzoylethylacetal;* it crystallises in well-developed hexagonal prisms, melts at 142°, and, with aniline, gives two or more compounds which will be described later. When reduced with hydriodic acid, a compound, $OH{\cdot}C_6Cl_2(OEt)(OBz)_2$, is formed; this crystallises in prisms, melts at 164°, and is being further investigated. *Dichlorodiethoxyquinol dibenzoate*, $C_6Cl_2(OEt)_2(OBz)_2$, prepared from sodium dichlorodiethoxyquinol and benzoic chloride, crystallises in long prisms, melts at 215°, and dissolves in hot concentrated sulphuric acid, but is not changed by hydrochloric acid, nitric acid, or alkali.

*Dichlorodimethoxyquinone dibenzoyldimethylacetal*,

$$C_6Cl_2(OMe)_4(OBz)_2,$$

prepared like the corresponding ethoxy-derivative (see above), crystallises in colourless plates, melts at 193°, and, when heated with dilute sulphuric acid, yields the *oxide* of *dichlorodimethoxyquinol dibenzoate*, $C_6Cl_2(OMe)_2(OBz)_2O$, which crystallises in rhombic prisms, melting at 205—206°. *Dichlorodiethoxyquinone diethylacetal ethylic dicarbonate*, $C_6Cl_2(OEt)_4(OCOOEt)_2$, prepared from the sodium salt of the hemiacetal and ethylic chlorocarbonate, crystallises in colourless, flat prisms melting at 122—123°.

*Tetraphenoxyquinone*, $C_6(OPh)_4O_2$, is readily obtained from dichlorodiphenoxyquinone and potassium phenoxide in aqueous solution; it is also formed from potassium phenoxide and chloranil in aqueous solution, and from sodium phenoxide and dichlorodiphenoxyquinone suspended in benzene, but in presence of alcohol, the diethoxydiphenoxy-derivative is obtained; it crystallises from benzene in red prisms, and melts at 229—230°. It is not changed by sulphurous acid at 100°, nor by sulphuric acid (sp. gr. = 1·44); hydriodic acid and stannous chloride in acid solution reduce it slowly, and it dissolves in concentrated sulphuric acid (sp. gr. = 1·83). *Diphenoxyanilic acid*, $C_6(OPh)_2(OH)_2O_2$, formed by heating the preceding compound with soda (1 : 4), crystallises in thick, lustrous, dark reddish-brown rectangular plates, softens at about 270°, and melts at about 276°. Acids are without action on it. The *sodium salt* forms black crystals which dissolve in water yielding a purple coloured solution.

*Tetraphenoxyquinol*, $C_6(OPh)_4(OH)_2$, is obtained when tetraphenoxyquinone is reduced by means of zinc dust and glacial acetic acid; it crystallises in colourless, well developed, thick, rhombic plates, commences to decompose at 210°, and melts at 219—220°. *Diethoxydiphenoxyquinone*, $C_6(OEt)_2(OPh)_2O_2$, is formed from dichlorodiphenoxyquinone and sodium phenoxide in absolute alcoholic solution (see above); it crystallises in long, silky, orange-yellow stellate needles, and melts at 128°. The yield is poor. *Dimethoxydiphenoxyquinone*, $C_6(OMe)_2(OPh)_2O_2$, prepared from tetraphenoxyquinone and sodium methoxide, crystallises in long, golden-yellow, prismatic needles, and melts at 171°. It is soluble in dilute soda; with sodium methoxide dissolved in methylic alcohol, it becomes white, dissolves in water, and, on the addition of dilute acid, a white, amorphous precipitate is produced which soon decomposes. A hemiacetal is probably formed, but it is much less stable than that derived from the dichloroquinone. *Dibromodiphenoxyquinone*, $C_6Br_2(OPh)_2O_2$, is prepared by the interaction of sodium phenoxide and bromanil in alcoholic solution, but probably an aqueous solution would be preferable; it crystallises in short, blunt, orange-red needles, melts at 266—267°, and is reduced by zinc dust and glacial acetic acid to the colourless quinol. Towards acids it is stable. Bromanil reacts with sodium phenoxide in alcoholic solution like chloranil in aqueous solution.

*Dibromodimethoxyquinone dimethylhemiacetal*, $C_6Br_2(OMe)_4(OH)_2$, formed from dibromodiphenoxyquinone and sodium methoxide, is white, amorphous, and melts at 178—188°; as it then becomes red, it is probably converted into dibromodimethoxyquinone; the same change is produced by dilute sulphuric acid or dilute hydrochloric acid.

*Chlorodiphenoxyquinone*, $C_6HCl(OPh)_2O_2$, is formed by the action of potassium phenoxide on trichloroquinone in aqueous solution; it crystallises in long, slender, oval, orange-coloured plates, melts at 169—170°, and, when treated with sodium methoxide, water, and dilute acid successively, it yields an unstable hemiacetal. Sodium ethoxide in alcoholic solution, when mixed with quinone dissolved in ether, gives a heavy, flocculent, dark green precipitate, which is decomposed by alcohol and water; when dried in air, it ignites spontaneously at the ordinary temperature, but if dried in hydrogen, and then exposed to air, it is stable up to 40°, but then burns like tinder; it is not a homogeneous substance, and in its production the constituents react in molecular proportion. The same compound, together with phenol, appears to be formed by the action of sodium ethoxide on phenoquinone. In order to ascertain whether phenoquinone is a hemiacetal, the action of sodium phenoxide on quinone was investigated; in presence of light petroleum a dark green precipitate is formed; with benzene as solvent, the precipitate is pink, and becomes dark green when heated; in ethereal solution, a dark red, crystalline compound is deposited; after removal of the ether, the residue readily dissolves in water with a slight green colour, and, when acidified, a dark red, crystalline substance is precipitated in small quantity. The subject is still under investigation.

J. B. T.

**Action of Bromine on Metanitraniline.** By Henry L. Wheeler (*Amer. Chem. J.*, 1895, **17**, 697—704).—The chief product formed by the action of bromine, in glacial acetic acid solution, on metanitraniline is *bromonitraniline* [$NH_2 : NO_2 : Br = 1 : 3 : 6$], which crystallises in bright yellow needles melting at 139—140°. Its constitution is shown by the formation of parabromonitrobenzene when it is treated with ethylic nitrite, and of dibromonitrobenzene $[NO_2 : Br : Br = 1 : 3 : 4]$ by means of Sandmeyer's reaction. The compound is volatile with steam, is less basic than the isomeride $[NH_2 : NO_2 : Br = 1 : 3 : 4]$, and, with strong acids, forms salts which are decomposed by water. The yield is 87·5 per cent. of the nitraniline employed; and by using metanitracetylanilide, this is increased to 111 per cent. The *hydrochloride* crystallises in colourless, lustrous scales melting and decomposing at about 200°. The *sulphate* is deposited in broad, thin, colourless, lustrous plates. The *acetyl derivative* crystallises in colourless, silky needles melting at 180°. Tribromonitraniline $[NH_2 : NO_2 : Br_3 = 1 : 3 : 2 : 4 : 6]$ is formed together with the preceding compound; the yield is 19 and 107 per cent. of the aniline and acetanilide respectively. Aniline, under the above conditions, yields chiefly di- and tri-bromo-derivatives, and when monobromoderivatives are formed, they are para- and not principally orthocompounds; in this instance, therefore, the nitro-group in the metaposition exerts a protective influence, and affects the position of the substituting atoms. J. B. T.

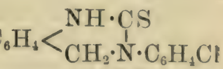
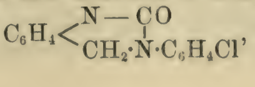
**A Correction (Bromination of Acetanilide and Acetoparatoluidide).** By WILHELM VAUBEL (*Ber.*, 1895, **28**, 3059).—The author points out that his observation regarding the bromination of acetanilide and acetoparatoluidide (Abstr., 1894, i, 19) is identical with that recorded by Blacher (*Ber.*, 1895, **28**, 2359).

M. O. F.

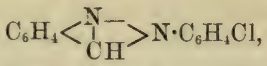
**Orthamidobenzylamine.** By MAX BUSCH (*J. pr. Chem.*, 1895, [2], **52**, 373—416; compare Abstr., 1895, i, 306—307).—X. With F. BRUNNER.—*Orthonitrobenzylorthochloraniline*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4Cl,$$

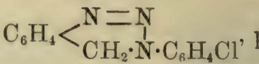
is prepared by heating orthonitrobenzylic chloride with orthochloraniline (2 mols.) for five hours in alcoholic solution, and is precipitated by adding water to the solution. It crystallises in yellow needles, melts at 67°, and dissolves easily in the usual solvents; the *hydrochloride* forms white needles, and melts at 172°. By reduction with zinc and acetic acid, the nitro-compound yields *orthamidobenzylorthochloraniline*, which crystallises in aggregates of yellowish needles, melts at 58°, and dissolves readily in ether and benzene, and in warm alcohol; the *hydrochloride* forms colourless needles, melts at 152°, and is soluble in water.

*3′-Orthochlorophenylthiotetrahydroquinazoline*,  $C_6H_4{<}\begin{matrix}NH\cdot CS\\ \mid\\ CH_2\cdot N\cdot C_6H_4Cl\end{matrix}$ (Abstr., 1894, i, 146), crystallises in white, silky laminæ, which become reddish on exposure to light, melt at 200°, and dissolve sparingly in the usual solvents. Reduction by means of sodium in alcohol converts it into 3-phenyltetrahydroquinazoline, and oxidation by mercuric oxide in alcohol at 150° converts it into *3′-orthochlorophenylketotetrahydroquinazoline*,  $C_6H_4{<}\begin{matrix}N — CO\\ \mid\\ CH_2\cdot N\cdot C_6H_4Cl\end{matrix}$, which crystallises in colourless laminæ, melts at 207°, and dissolves in alcohol and, sparingly, in ethylic acetate.

XI. With FRANCIS E. FRANCIS.—*Orthonitrobenzylmetachloraniline* forms yellow crystals, melts at 59°, and dissolves easily in glacial acetic acid, alcohol, ether, and benzene, but sparingly in light petroleum, and not at all in water. *Orthamidobenzylmetachloraniline* is an oil; its *hydrochloride* crystallises in white laminæ, melts at 137—138°, and is sparingly soluble in water, although freely soluble in alcohol.

*Metachlorophenylindazole*,  $C_6H_4<\overset{N-}{\underset{CH}{|}}>N\cdot C_6H_4Cl$, also produced during the reduction of orthonitrobenzylmetachloraniline, crystallises in large, white laminæ, melts at 110°, and dissolves easily in ether, benzene, and chloroform, but only sparingly in cold alcohol.

3′-*Metachlorophenylthiotetrahydroquinazoline* crystallises in colourless, vitreous needles, melts at 198—199°, and is sparingly soluble save in glacial acetic acid and chloroform; reduction only affects the chlorine, 3′-phenylthiotetrahydroquinazoline being formed.

*Metachlorophenyldihydro-β-phenotriazine*,  $C_6H_4\left\langle\begin{array}{l}N{=}N\\CH_2\cdot\overset{|}{N}\cdot C_6H_4Cl\end{array}\right.$, prepared by the action of amylic nitrite on an alcoholic solution of orthamidobenzylmetachloraniline hydrochloride, crystallises in yellow needles, melts and evolves gas at 146—147°, and dissolves easily in benzene, ether, and hot alcohol, sparingly in light petroleum.

XII. With C. VOLKENING.—Orthonitrobenzylparachloraniline has been already described (Abstr., 1894, i, 210); the *hydrochloride* melts at 170—172°; the *sulphate* is described. *Orthamidobenzylparachloraniline* crystallises in lustrous, white needles, melts at 89—90°, and is freely soluble in most organic solvents; a *hydrochloride* and a *dihydrochloride* are described.

The *benzylidene* derivative, $CHPh\colon N\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4Cl$, formed by heating orthamidobenzylparachloraniline with benzaldehyde in alcohol, crystallises in stellate groups of white needles, melts at 115—116°, and dissolves easily in hot benzene and alcohol, but only sparingly in ether or light petroleum. The *orthohydroxybenzylidene* derivative crystallises in stellate groups of yellow prisms, melts at 124°, and is soluble in the usual solvents. The *metanitrobenzylidene* derivative melts at 86°, and is sparingly soluble in alcohol, ether, and chloroform, more so in benzene and glacial acetic acid, and insoluble in light petroleum. *Orthacetamidobenzylparachloraniline*, $NHAc\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4Cl$, prepared by heating the base with acetic anhydride, crystallises in long, colourless prisms, melts at 188°, and dissolves freely in hot benzene, chloroform, and carbon bisulphide.

3′-*Parachlorophenylthiotetrahydroquinazoline* crystallises in lustrous, white laminæ, melts at 228°, and is soluble in the usual solvents, except carbon bisulphide and boiling glacial acetic acid. *Parachlorophenyldihydro-β-phenotriazine* crystallises in yellow laminæ, and also in thick crystals; it melts at 134°, and dissolves easily in benzene and chloroform, but only sparingly in ether or light petroleum; the *hydrochloride*, $C_{13}H_{10}N_3Cl,HCl$, melts and explodes at 103°, and is soluble in alcohol, but is dissociated by water; the *platinochloride*, *aurochloride*, and *picrate* are described.

*Parachlorophenylorthonitrobenzylnitrosamine*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot N(NO)\cdot C_6H_4Cl,$$

crystallises in yellow, transparent prisms, melts at 100°, and dissolves freely in benzene, glacial acetic acid, and hot alcohol, but only sparingly in ether or light petroleum.

*Parachlorophenylorthamidobenzylhydrazine*,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot N(NH_2)\cdot C_6H_4Cl,$$

forms crystals, and melts at 95°; it dissolves in most solvents, and yields a *benzylidene* derivative, $CHPh\colon N\cdot C_6H_4\cdot CH_2\cdot N(N\colon CHPh)\cdot C_6H_4Cl$, when heated with benzaldehyde and alcohol; this crystallises in long, felted needles, melts at 150°, and dissolves easily in ether, benzene, carbon bisulphide, and chloroform, but only sparingly in alcohol.

XIII. With FR. HEINEN.—Orthamidobenzylparabromaniline has been already described (Abstr., 1894, i, 210); the *dihydrochloride* melts at 93—94°, and the *oxalate* at 127°; the *benzylidene* derivative (*benzylideneorthamidobenzylparabromaniline*) crystallises in stellate groups of white needles, melts at 122°, and dissolves freely in chloroform, carbon bisulphide, and glacial acetic acid, but only sparingly in ether, alcohol, benzene, or light petroleum; the *orthohydroxybenzylidene* derivative crystallises in yellow prisms, melts at 143—144°, and is soluble in most solvents; the *paranitrobenzylidene* derivative melts at 144°, and is sparingly soluble in the usual solvents, except glacial acetic acid and benzene. *Orthacetamidobenzylparabromaniline* crystallises in colourless prisms, melts at 138°; it is easily soluble in benzene and chloroform, but very sparingly in ether and light petroleum.

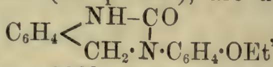
3′-*Parabromophenylketotetrahydroquinazoline*, from carbonyl chloride and orthamidobenzylparabromaniline, crystallises in transparent, quadratic tablets, melts at 226°, and is sparingly soluble in alcohol, ether, carbon bisulphide, and light petroleum, but freely in boiling benzene, glacial acetic acid, and chloroform. *Parabromophenylthiotetrahydroquinazoline* forms long, colourless, four-sided prisms, melts at 234°, and dissolves easily in amylic alcohol.

*Parabromophenyldihydro-β-phenotriazine* crystallises in lustrous, yellow laminæ, melts at 164°, and dissolves freely in benzene, alcohol, ether, chloroform, and carbon bisulphide, sparingly in light petroleum, and not at all in water; the *hydrochloride* melts at 105—106°; the *platinochloride* (m. p. 191°), *aurochloride* (m. p. 108—109°), and *picrate* (m. p. 106°), are described.

*Parabromophenylorthonitrobenzylnitrosamine*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot N(NO)\cdot C_6H_4Br,$$

formed by the action of nitrous acid on orthonitrobenzylparabromaniline, crystallises in microscopic tables, melts at 167°, and dissolves easily in the usual solvents, except light petroleum. *Parabromophenylorthamidobenzylhydrazine* crystallises in lustrous tables, melts at 119—120°, and dissolves freely in the usual solvents, except light petroleum; the *oxalate* melts at 135°; the *benzylidene* derivative, $CHPh\colon N\cdot C_6H_4\cdot CH_2\cdot N(N\colon CHPh)\cdot C_6H_4Br$, crystallises in long, colourless prisms, melts at 171°, and dissolves in most solvents.

XIV. With PAUL HARTMANN. — *Orthamidobenzylparaphenetidine*, from orthonitrobenzylparaphenetidine (*loc. cit.*), crystallises in nacreous laminæ, melts at 78°, and dissolves in alcohol, ether, benzene, chloroform, and glacial acetic acid; the *hydrochloride*, *sulphate* (m. p. 100°), *oxalate* (m. p. 132°), *benylidene* derivative (m. p. 137°), and *orthohydroxybenzylidene* derivative (m. p. 94°), are described. *3'-Phenetylketotetrahydroquinazoline*,  $C_6H_4{<}\begin{matrix}NH-CO\\ \quad\;\; | \\ CH_2\cdot N\cdot C_6H_4\cdot OEt\end{matrix}$, crystallises in colourless needles, and melts at 223°; it dissolves in glacial acetic acid, ethylic acetate, and chloroform, sparingly in ether and benzene, and not at all in water or light petroleum. *3'-Phenetylthiotetrahydroquinazoline* crystallises in white, silky needles, melts at 238°, and dissolves sparingly in the usual organic solvents, but not in ether, light petroleum, or water. 3'-Paraphenetyltetrahydroquinazoline melts at 129°, not 124° (*loc. cit.*).

*Paraphenetyldihydro-β-phenotriazine* crystallises in yellow laminæ, melts at 144°, and is soluble in the usual solvents, except light petroleum; the *hydrochloride* (m. p. 115°), *platinochloride*, *aurochloride*, *hydrobromide* (m. p. 104°), and *picrate* are described.

XV. With F. BRUNNER and RUD. BIRK.—*Orthonitrobenzylorthanisidine*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot OMe$, forms brilliant, thick, orange-red crystals, and melts at 80°.

*Orthamidobenzylorthanisidine* crystallises in colourless needles, and melts at 99°; the *dihydrochloride* melts at 175—176°.

*Azo-orthobenzylorthanisidine*, $(OMe\cdot C_6H_4\cdot NH\cdot CH_2\cdot C_6H_4)_2N_2$, crystallises in orange needles, melts at 150—151°, and dissolves easily in benzene, sparingly in ether.

*Orthohydroxybenzylideneorthamidobenzylorthanisidine*,

$$OH\cdot C_6H_4\cdot CH\colon N\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot OMe,$$

from salicylaldehyde and orthamidobenzylorthanisidine, crystallises in yellow, silky needles, and melts at 79°.

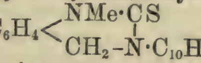
*3'-Orthomethoxyphenylketotetrahydroquinazoline* melts at 217—218°, and *3'-orthomethoxyphenylthiotetrahydroquinazoline* at 237°.

XVI. With PAUL HARTMANN.—*Orthamidobenzylparanisidine* melts at 82°; *paranisyldihydro-β-phenotriazine* melts at 139°; both dissolve in most solvents; the *hydrochloride*, *platinochloride*, and *picrate* (m. p. 125°) of the triazine are described.

XVII. With FR. BRAND.—*Orthamidobenzyl-α-naphthylamine*,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_{10}H_7,$$

crystallises in lustrous, reddish laminæ, melts at 134°, and dissolves in benzene easily, and in alcohol, ether, and light petroleum with difficulty; the solutions have a bluish-red fluorescence; the *dihydrochloride*, the *sulphate*, $C_{17}H_{16}N_2(H_2SO_4)_2$, the *benzylidene* derivative (m. p. 107°), and the *orthohydroxybenzylidene* derivative (m. p. 162°) are described.

*3'-α-Naphthylthiotetrahydroquinazoline* crystallises in colourless, lustrous laminæ, melts at 255°, and dissolves easily in xylene, amylic alcohol, and chloroform; the 1′-*methyl derivative*,  $C_6H_4<\begin{array}{l}NMe\cdot CS\\ \qquad\quad | \\ CH_2-N\cdot C_{10}H_7\end{array}$, formed by the action of methylic iodide on the quinazoline, crystallises in white needles; its *hydriodide* blackens and melts at 212°.

XVIII. With Fr. Brand.—*Orthonitrobenzyl-β-naphthylamine*, from β-naphthylamine and orthonitrobenzylic chloride, crystallises in lustrous, red laminæ, melts at 162°, and dissolves in the usual solvents, save chloroform; the *hydrochloride* is described. *Orthamidobenzyl-β-naphthylamine* forms white, lustrous laminæ, melts at 99°, and dissolves like the α-compound; the *benzylidene* derivative (m. p. 122°), *orthohydroxybenzylidene* derivative (m. p. 117°), and methylene derivative (m. p. 155—158°) are described. *Orthoacetamidobenzyl-β-acetonaphthalide*, $NHAc\cdot C_6H_4\cdot CH_2\cdot NAc\cdot C_{10}H_7$, forms colourless, thick crystals, melts at 116°, and dissolves sparingly in ether, benzene, and glacial acetic acid, but not in light petroleum.

3′-*β-Naphthylthiotetrahydroquinazoline* crystallises in thick, colourless laminæ, melts at 280°, and dissolves freely in glacial acetic acid and amylic alcohol; the 1′-*methyl* derivative melts at 140°, and its *hydriodide* decomposes and melts at 249°.

*Orthonitrobenzyl-β-naphthylnitrosamine* crystallises in dark yellow, thick laminæ, melts at 102°, and dissolves freely in benzene, glacial acetic acid, and chloroform. *Orthamidobenzyl-β-naphthylhydrazine*, prepared by the reduction of the nitrosamine, crystallises in slender needles, and melts at 76°; its *orthohydroxybenzylidene* derivative, $OH\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot CH_2\cdot N(N{:}CH\cdot C_6H_4\cdot OH)\cdot C_{10}H_7$, crystallises in yellow, felted needles, melts at 176°, and dissolves freely in benzene, glacial acetic acid, and chloroform. A. G. B.

**Derivatives of Dimethylparatoluidine.** By Johannes Pinnow (*Ber.*, 1895, **28**, 3039—3045; compare Abstr., 1895, i, 98).—*Orthonitroparatolylmethylnitrosamine* is obtained by adding aqueous sodium nitrite to orthonitrodimethylparatoluidine dissolved in hydrochloric acid; it crystallises from alcohol in yellow needles or prisms, and melts at 55°. *Orthonitromethylparatoluidine* is formed when methylparatoluidine is nitrated in sulphuric acid solution, the liquid being subsequently treated with sodium nitrite at 0°; it crystallises in red needles or prisms, melting at 57°, and the *acetyl* derivative crystallises in slender, yellow needles melting at 128—128·5°. *Methylorthonitroparatolylnitramine* is isolated from the liquid containing orthonitroparatolylmethylnitrosamine; it crystallises from acetone in red prisms with green reflex, and melts at 184·5—185·5° (uncorr.). An ethereal extract of the liquid, when treated with sodium carbonate, yields *dinitrodimethylparatoluidine*, which crystallises from alcohol in red, lustrous leaflets, and melts at 103·5—104°.

*Metanitrodimethylparatoluidine* is also formed by the action of nitrous acid on dimethylparatoluidine, and is obtained as a dark red oil, which does not solidify at −15°. *Amidodimethylparatoluidine*, produced when the nitro-compound is reduced with tin and hydrochloric acid, is a colourless oil, which boils at 234° (uncorr.) under a pressure of 759 mm.; the *hydrochloride* and *mercurichloride* melt at 192—193° and 205—206° respectively, whilst the *picrate* crystallises from alcohol in brownish-yellow prisms, and melts at 150·5°. The action of boiling acetic anhydride during four hours converts the base into methylethenyltolulylenamidine (Niementowski, Abstr., 1887, 937); the *acetyl* derivative of amidodimethylparatoluidine is obtained by the action of glacial acetic acid during eight hours, and melts at 111·5—112·5°. The *phenylthiocarbamide* crystallises in prisms, and melts at 153—154° (uncorr.).

In addition to amidodimethylparatoluidine, reduction of metanitrodimethylparatoluidine gives rise to a *compound* which crystallises in white needles, and yields a *picrate*, crystallising from amylic alcohol in yellow leaflets, and melting at 254·5° (uncorr.).

When nitrous gas is led into a solution of dimethylparatoluidine in nitric acid, methyldinitrotolylnitrosamine (Gattermann, Abstr., 1885, 975) is formed; it is also obtained by the action of nitric acid on methyltolylnitrosamine dissolved in glacial acetic acid.

M. O. F.

**Synthetical Use of Iodine Chloride.** By M. KERSCHBAUM (*Ber.*, 1895, **28**, 2798—2804).—*as*-Metaxylidine is converted by 1 mol. of iodine chloride, ICl, into *orthoiodometaxylidine*, $[Me_2 : NH_2 : I = 1 : 3 : 4 : 5]$; the base crystallises in colourless needles, melting at 65°. The *hydrochloride* is only sparingly soluble in water, whilst the *nitrate* and *sulphate* are more readily soluble. The *acetyl* compound forms lustrous white plates melting at 85°. The *nitrile* crystallises in yellowish needles, and melts at 135°. It has not yet been found possible to convert this substance by hydrolysis into an acid.

When 2 mols. of iodine chloride react with metaxylidine, the iododerivative is accompanied by a small amount of *tetramethylorthodiamidodiphenyl* $[Me_4 : (NH_2)_2 = 3 : 5 : 3' : 5' : 2 : 2']$, which is formed from the xylidine by condensation. It crystallises in small, rhombic tablets, melts at 180°, and may be distilled in small quantities, almost without decomposition. The *hydrochloride* and *sulphate* are readily soluble; the *nitrate* is sparingly soluble, and crystallises in large, white prisms. The *diacetyl* compound forms small plates, and melts at 210°. The base can readily be diazotised, and yields colouring matters with α- and β-naphthol, &c. *Tetramethyldiphenylimide* (tetramethylcarbazole), $C_6H_2Me_2{<}\overset{NH}{\underline{\qquad}}{>}C_6H_2Me_2$, is formed when the tetrazo-solution is treated with potassium sulphide. It crystallises in small plates, melts at 128—129°, and, like carbazole, forms a yellow solution in sulphuric acid, turned green by nitric acid. It is insoluble in water, but readily soluble in alcohol, &c. The *picrate* forms reddish-brown needles.

No analogous compounds have been obtained from other bases by the action of 2 mols. of iodine chloride.

A. H.

**Amido-derivatives of Paraxylene.** By FRANZ LUSTIG (*Ber.*, 1895, **28**, 2986—2994).—Paramethylbenzylphthalimide,

$$C_6H_4Me{\cdot}CH_2{\cdot}N{:}C_8H_4O_2,$$

and paraxylylene-exo-diphthalimide were obtained by treating with potassium phthalimide the mixture of mono- and di-bromoparaxylenes with the dibromide [$C_6H_4Me{\cdot}CH_2Br$ and $C_6H_4(CH_2Br)_2$] obtained by the bromination in sunlight of cold paraxylene; they were separated by extraction with cold carbon bisulphide in which the monophthalimide alone is soluble. The monophthalimide yields paramethylbenzylphthalamic acid when hydrolysed with alcoholic potash, and paramethylbenzylamine when hydrolysed with a mixture of acetic and concentrated hydrochloric acids at 150—160°. Paramethylbenzylamine picrate melts at 204° (Kröber, Abstr., 1890, 968, gives 194—199°), the acetyl derivative at 107—108° (Kröber, 106·5°), and the benzoyl compound at 137° (Kröber, 125°).

*Metanitroparamethylbenzylbenzamide*, $NO_2{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}NHBz$, is obtained when the above benzoyl derivative is dissolved in sulphuric acid, and then treated with a mixture of nitric and sulphuric acids. It crystallises in colourless needles, melts at 145—147°, and when hydrolysed with hydrochloric acid, yields benzoic acid and *nitroparamethylbenzylamine hydrochloride;* the *platinochloride*,

$$(NO_2{\cdot}C_8H_8{\cdot}NH_2)_2,H_2PtCl_6,$$

forms an orange red, crystalline powder, and decomposes at 231°; the *picrate* crystallises in short, bright yellow needles, and melts and decomposes at 211°.

The benzoyl compound, when reduced with zinc and hydrochloric acid, according to Gabriel and Jansen's method (Abstr., 1890, 1442), yields *metamidoparamethylbenzylbenzamide*, which crystallises from water in colourless needles, and melts at 113—115°. Since it is not converted into an anhydride by heating to 300°, nor by distillation, it is probable that the amide group is not in the ortho-position relatively to the $CH_2{\cdot}NHBz$-group. The amido-compound must therefore be $NH_2{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}NHBz$ [= 3 : 4 : 1]. The *hydrochloride* decomposes and melts at 237°, the *picrate* turns brown, and melts at 170—171°, and the *chromate* forms yellowish-red needles, which decompose at 80°. The benzoyl compound, when hydrolysed with hydrochloric acid at 150°, yields *metamidoparamethylbenzylamine hydrochloride;* this crystallises in colourless needles, melts with decomposition at 285°, and yields a *picrate*, which also decomposes at 285°.

*Paraxylylene-exo-diphthalimide*, $C_6H_4(CH_2{\cdot}N{:}C_8H_4O_2)_2$, is insoluble in alcohol, ether, chloroform, benzene, and acetic acid, but crystallises from nitrobenzene in small, white needles; it melts at 279—280°, and, when hydrolysed with alcoholic potash, yields *paraxylylene-exo-diphthalamic acid*, $C_6H_4(CH_2{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}COOH)_2$, which, when heated to 279°, loses water, and is converted back again into the diphthalimide.

*Nitroparaxylene-exo-diphthalimide* crystallises from nitrobenzene in colourless needles, and melts at 253—255°.

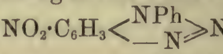
*Paraxylylene-exo-diamine hydrochloride*, $C_6H_4(CH_2{\cdot}NH_2,HCl)_2 + 1\frac{1}{2}H_2O$, obtained by the hydrolysis of the diphthalimide with concentrated hydrochloric acid, crystallises in colourless needles; the *platinochloride* decomposes at 250°, and the *picrate*, which crystallises in large, orange needles, at 232°.

The *tetracetyl derivative*, $C_6H_4(CH_2\cdot NAc_2)_2$, crystallises in colourless needles and melts at 194°, and the *dibenzoyl* derivative at 193—194°.

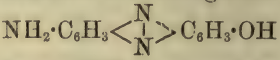
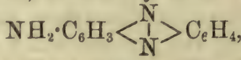
*Nitroparaxylylene-exo-diamine hydrochloride*, obtained from the nitroparaxylylene-exo-diphthalimide, crystallises with $1\frac{1}{2}H_2O$, and decomposes when heated for some time at 160°. The *platinochloride* decomposes at 295°, and the *picrate* at 237°.

*Nitroparaxylylene-exo-dibenzamide*, obtained by the action of benzoic chloride on the nitro-base, crystallises in colourless needles, and melts at 210·5—211°. J. J. S.

### Amido-derivatives of Diphenylamine and their relation to Indamines and Azines. By Rudolf Nietzki (*Ber.*, 1895, **28**, 2969—2981).

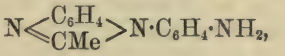
—I. With Karl Almenräder.—2 : 4-Dinitrodiphenylamine, $NHPh\cdot C_6H_3(NO_2)_2$, is best reduced by iron filings and 2 per cent. hydrochloric acid, the liquid being finally treated with excess of sodium carbonate. The diamido-compound forms brownish needles and melts at 130°; its salts are very unstable; it does not condense to an azine, exhibits the behaviour of a meta-diamine, and yields a colourless *diacetyl derivative* melting at 188°. Warm alcoholic ammonium sulphide reduces the dinitro-compound partially to red *nitramidodiphenylamine*, $NHPh\cdot C_6H_3(NH_2)\cdot NO_2$ [1 : 2 : 4]; this melts at 125°, and yields a *monacetyl derivative* melting at 163—164°. Nitrous acid converts it into a yellowish *azimide*,  $NO_2\cdot C_6H_3<\begin{smallmatrix}NPh\\ \_\_N\end{smallmatrix}\geqslant N$, which melts at 107°, and can be reduced with stannous chloride to the colourless *amido-derivative*, which melts at 159° and forms a *platinochloride*, and a *monacetyl derivative* melting at 266°.

II. With Carl Simon.—1 : 2 : 4-Diamidodiphenylamine is oxidised by manganese dioxide in very dilute ammoniacal solution to a yellowish-brown compound, $C_{12}H_{10}N_2O$, of undetermined constitution, melting at 152°.

2 : 4-*Dinitro-4′-hydroxydiphenylamine*, $C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4\cdot OH$, was prepared by the action of paramidophenol on dinitrochlorobenzene; it is red, and melts at 190°; its yellow *monacetyl derivative* melts at 129°. It can be reduced by stannous chloride to the *diamido-compound*, which forms a rather unstable *monohydrochloride* and readily oxidises in the presence of air to the dark-coloured diamidoindophenol, $C_6H_3(NH_2)_2\cdot N\colon C_6H_4\colon O + 2H_2O$ [$(NH_2)_2 : OH = 2 : 4 : 4'$], which melts at 133° when anhydrous. If the hydrochloride is oxidised with manganese peroxide, yellow *amidohydroxyphenazine*,  $NH_2\cdot C_6H_3<\overset{N}{\underset{N}{|}}>C_6H_3\cdot OH$ [$NH_2 : OH = 3 : 3'$], is obtained; this melts at 268°, its greenish-yellow *diacetyl derivative* at 258°. 2 : 4-*Diamido-2′-hydroxydiphenylamine* was prepared by reducing the corresponding dinitro-compound; it was not isolated on account of its extreme instability, but was at once oxidised, when it yielded O. Fischer and Hepp's red 3-amidophenazine,  $NH_2\cdot C_6H_3<\overset{N}{\underset{N}{|}}>C_6H_4$, melting at 265°.

III. With Otto Baur.—The red dinitrodiphenylamine obtained by

Witt (*Ber.*, **11**, 758) is shown to be the 2 : 4′-dinitro-compound, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$. It can be made from 1 : 4-mononitrodiphenylamine, and so contains one nitro-group in the para-position; that the second is in the ortho-position is shown by the conversion into a phenazine, and other reactions described below. Partially reduced, it yields a nitramido-compound, which is reddish-brown with a shimmer of blue, and melts at 144°; this yields a yellow *monacetyl derivative* melting at 178°; with nitrous acid, it yields a yellow *nitroazimide* melting at 239°, that can be reduced with stannous chloride to a colourless *amido-compound* melting at 134·5°, the *monacetyl derivative* of which melts at 200°. The diamido-compound obtained by complete reduction of dinitrodiphenylamine (Nietzki and Witt, *Ber.*, **12**, 1399) readily oxidises to the red amidophenazine melting at 265°. Its acetyl derivative, when heated at 120° with strong hydrochloric acid, does not regenerate the diamido-base, as was formerly supposed, but yields the *ethenyl derivative*,



$$\mathrm{N}{<}\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CMe}\end{matrix}{>}\mathrm{N{\cdot}C_6H_4{\cdot}NH_2},$$

the acetyl derivative of which melts at 219°.

IV. The following general conclusions are drawn as to the behaviour of the amidodiphenylamines. (1) To get an indamine, the para-positions in both benzene nuclei must be occupied. (2) Azines are formed when a para-position is occupied in one nucleus, and an ortho-position in the other, and no indamine is then formed as an intermediate product. If one nucleus has no substituting groups, or only one in the meta-position, neither an indamine nor an azine is formed. (3) If the ortho-positions in both nuclei are occupied, one of the occupying groups ($NH_2$ or OH) is lost when the phenazine is formed.

C. F. B.

**Preparation of Orthophenylenediamine.** By Oscar Hinsberg and Fritz König (*Ber.*, 1895, **28**, 2947).—Fifty grams of orthonitraniline is dissolved in 100—150 c.c. of boiling alcohol, 40 c.c. of 20 per cent. aqueous caustic soda added, and then zinc dust is introduced fairly rapidly in small portions at a time. When the addition of zinc dust seems to produce no further action, 10 c.c. more caustic soda is added, and the addition of zinc dust continued as before; this proceeding should be repeated once or twice. In about an hour, the reddish-yellow colour of the solution will have changed to a pale brown, and the action will be complete. The solution is then filtered, the residue extracted twice with boiling alcohol, and the filtrate and washings evaporated in a current of hydrogen until all the alcohol has been driven off. The residue of orthophenylenediamine is broken up when cold, dried on a porous plate, and distilled; the yield is 90 per cent. of the theoretical. Other amidonitro-compounds can be reduced conveniently in the same manner; not, however, alkyl derivatives of orthonitraniline. C. F. B.

**Action of Ethylic Orthoformate on Primary Aromatic Amines.** By R. Walther (*J. pr. Chem.*, 1895, [2], **52**, 429—430).—

This reaction yields amidines very easily at the temperature of the water bath in the majority of cases (compare Claisen, this vol., i, 91). The following were obtained: *Methenyldiphenylamidine*, silvery laminæ or prisms, m. p. 138—139°. *Methenyldiorthonitrophenylamidine*, brilliant, golden needles, m. p. 124—125°. *Methenyldimetanitrophenylamidine*, soft, felted needles, m. p. 198—199°. *Methenyldiparanitrophenylamidine*, golden laminæ, m. p. 236—237°. *Methenyldiorthotolylamidine*, lustrous, white laminæ, or thick, transparent crystals, m. p. 149°. *Methenyldiparatolylamidine*, white laminæ or large, transparent prisms, m. p. 141°; the *acetate* crystallises in white needles. *Formazyl hydride*, obtained by the action of ethylic orthoformate on phenylhydrazine, forms violet crystals, m. p. 117°; from light petroleum, it separates as a red, crystalline mass (containing petroleum of crystallisation), which melts at 114°. *Methenyldimetabromophenylamidine*, silvery laminæ or stout prisms, m. p. 135°. *Methenylditribromophenylamidine*, long, white needles, m. p. 78°.

The compound from amidoazobenzene forms long, brownish-red prisms or slender needles, and melts at 191—193°; that with picramic acid is a moss-green powder, melting at 183—184°, and is absolutely insoluble. A. G. B.

**Quinazine and Oxazine Colouring Matters.** By RICHARD MÖHLAU and KARL UHLMANN (*Annalen*, 1895, **289**, 90—130; compare Abstr., 1892, 887, and 1893, i, 44).—The authors accept the modification in the nomenclature of these colouring matters which has been put forward by Nietzki and Bossi (*loc. cit.*), and they also adopt the expressions *azime* and *azone* for indamine and indophenol derivatives respectively; thus reference is made to phenylene-blue and α-naphthol-blue as amidodiphenazime and dimethylamidophenonaphthazone.

*Dibromodimethylamidodiphenazone*, $\overset{4}{O}{:}C_6H_2\overset{3,5}{Br_2}{:}\overset{1}{N}\cdot C_6H_4\cdot\overset{4}{N}Me_2$, obtained by adding dimethylaniline (2 mols.) to an alcoholic solution of dibromoquinonechlorimide saturated at 30°, separates in green prisms which appear blue by transmitted light; when heated on platinum foil, it decomposes without undergoing fusion. The dye is insoluble in water, but dissolves sparingly in cold alcohol and ether, yielding greenish-blue solutions, whilst hot alcohol, aniline, and pyridine dissolve it readily. Dimethylamidodibromodiphenazone is hydrolysed by boiling dilute hydrochloric acid, yielding ammonia, dimethylaniline, dibromoparamidophenol, dibromoquinone, and quinone, whilst boiling caustic soda gives rise to hydroxydibromodiphenazone and dimethylaniline.

*Sodium dibromodiphenazone-orthohydroxycarboxylate*,

$$\overset{4}{O}{:}C_6H_2\overset{3,5}{Br_2}{:}\overset{1}{N}\cdot C_6H_2\overset{4}{(ONa)}\cdot\overset{3}{COONa},$$

is obtained on agitating dibromoquinonechlorimide (15 grams) dissolved in ether (300 c.c.) with a solution (135 c.c.) containing 5 grams of salicylic acid and 4·4 grams of caustic soda in 100 c.c. of water; it dissolves readily in water and alcohol, yielding blue liquids, but is insoluble in ether. Concentrated sulphuric acid dissolves it, forming an orange-yellow solution, which becomes purple, and ultimately colourless, on dilution with water. The *acid* is liberated in the form of a brownish-red powder, which dissolves sparingly in water and chloroform, being readily soluble in acetone, alcohol, and ether.

*Dibromodihydroxydiphenylaminecarboxylic acid*,

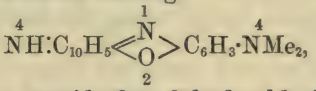
$$\overset{4}{\mathrm{O}}\mathrm{H}\cdot \mathrm{C_6H_2}\overset{3,5}{\mathrm{B}}\mathrm{r_2}\cdot\overset{1}{\mathrm{N}}\mathrm{H}\cdot\mathrm{C_6H_3}(\overset{4}{\mathrm{O}}\mathrm{H})\cdot\overset{3}{\mathrm{C}}\mathrm{OOH},$$

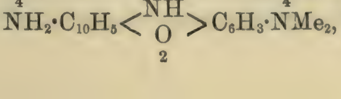
the leuco-derivative of the foregoing compound, is obtained from it by reduction with grape sugar or zinc and alkali; it crystallises from acetone in needles, and melts and decomposes at 209°. The substance is insoluble in water and chloroform, dissolving in ether, alcohol, pyridine, and acetone; the solution in caustic soda rapidly undergoes oxidation when exposed to air.

The *sodium* derivative of *dibromohydroxynaphthadiphenazone*,

$$\overset{4}{\mathrm{O}}\mathrm{:C_6H_2}\overset{3,5}{\mathrm{B}}\mathrm{r_2:}\overset{1}{\mathrm{N}}\cdot\mathrm{C_{10}H_6}\cdot\overset{4}{\mathrm{O}}\mathrm{Na},$$

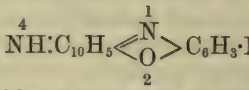
produced by the action of dibromoquinonechlorimide on an alkaline solution of α-naphthol, crystallises in blue needles with green reflex; it yields a blue solution with water and alcohol, but is insoluble in ether. When the sodium derivative absorbs carbonic anhydride, *dibromohydroxynaphthadiphenazone* is produced; this melts at 201° without decomposing. Hot dilute mineral acids resolve it into dibromoparamidophenol, dibromoquinone, and 1 : 4-amidonaphthol. *Dibromohydroxyphenylhydroxynaphthylamine*, the leuco-derivative of the foregoing compound, is obtained by reducing it in alcoholic solution with grape sugar and caustic soda; it crystallises in lustrous, white leaflets, and decomposes at 152° without melting.

*Dimethylamidophenonaphthoxazime*,  $\overset{4}{\mathrm{N}}\mathrm{H:C_{10}H_5}<\begin{matrix}\overset{1}{\mathrm{N}}\\ \underset{2}{\mathrm{O}}\end{matrix}>\mathrm{C_6H_3}\cdot\overset{4}{\mathrm{N}}\mathrm{Me_2}$, is prepared by adding nitrosodimethylmetamidophenol hydrochloride (17 grams) to a boiling 10—15 per cent. solution of α-naphthylamine hydrochloride (10 grams) in acetic acid containing 20 per cent. of water; this operation yields the *hydrochloride*, which crystallises from boiling water acidified with a few drops of hydrochloric acid, in small needles; it appears green by transmitted, and violet by reflected light. The dye forms a blue solution in water, alcohol, and pyridine, and the solution in concentrated sulphuric acid is orange-red, becoming green and blue successively on dilution with water; owing to its constitutional relation to the well-known dye, the authors refer to it as "methyl Nile blue." The *base* is liberated when caustic soda is added to the dye suspended in absolute alcohol until the colour is changed from blue to red; it crystallises in reddish-brown needles which contain water, and become anhydrous at 120°. It decomposes before melting, and yields fluorescent liquids with common organic solvents. Reduction with zinc and hydrochloric acid converts the base into the *zincochloride* of the leuco-derivative, dimethyldiamidonaphthaphenoxazine,

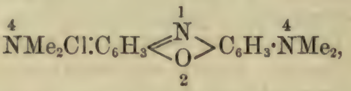


$$\overset{4}{\mathrm{N}}\mathrm{H_2}\cdot\mathrm{C_{10}H_5}<\begin{matrix}\overset{1}{\mathrm{N}}\mathrm{H}\\ \underset{2}{\mathrm{O}}\end{matrix}>\mathrm{C_6H_3}\cdot\overset{4}{\mathrm{N}}\mathrm{Me_2},$$

which crystallises in greenish-white needles; it is rapidly oxidised on exposure to air.

*Diethylamidophenonaphthoxazime*,  $\overset{4}{\mathrm{N}}\mathrm{H}{:}\mathrm{C_{10}H_5}{<}\begin{matrix}\overset{1}{\mathrm{N}}\\ \underset{2}{\mathrm{O}}\end{matrix}{>}\mathrm{C_6H_3}\cdot\overset{4}{\mathrm{N}}\mathrm{Et_2}$, which the authors refer to as "ethyl Nile blue," is prepared from nitrosodiethylmetamidophenol; it is obtained as the *hydrochloride*, which crystallises in lustrous, green needles, appearing blue by transmitted light; the salt is sparingly soluble in cold water, but dissolves readily in hot water, alcohol, and pyridine, yielding a blue solution. The *base* crystallises in green needles, which are brown by transmitted light; it is insoluble in water, but dissolves in common organic solvents, yielding fluorescent liquids. Reduction with zinc and hydrochloric acid gives rise to the *zincochloride* of the leuco-derivative, crystallising in white needles, which dissolve in water and are readily oxidised on exposure to air.

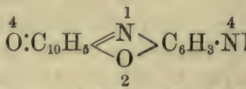
*Tetramethylamidodiphenoxazimium chloride*,



$$\overset{4}{\mathrm{N}}\mathrm{Me_2Cl}{:}\mathrm{C_6H_3}{<}\begin{matrix}\overset{1}{\mathrm{N}}\\ \underset{2}{\mathrm{O}}\end{matrix}{>}\mathrm{C_6H_3}\cdot\overset{4}{\mathrm{N}}\mathrm{Me_2},$$

is obtained by adding nitrosodimethylmetamidophenol hydrochloride (20·2 grams) to a boiling solution of dimethylmetamidophenol (13·7 grams) in glacial acetic acid (150 grams); owing to its high degree of solubility in water, it is convenient to convert the chloride into the *iodide* by gradually adding hydrochloric acid in quantity sufficient to liberate the requisite amount of hydriodic acid from potassium iodide, and treating the boiling liquid with an aqueous solution of this salt. The iodide crystallises in blue needles having a green reflex, and contains $1H_2O$, which is removed in a vacuum; the solutions in water, acetone, and chloroform are blue, and exhibit strong brownish-red fluorescence.

*Tetrethylamidodiphenoxazimium iodide* is prepared from nitrosodiethylmetamidophenol hydrochloride by treating the *chloride* in the manner described; it crystallises from alcohol in blue needles having a vivid green reflex. The solutions of the iodide resemble those of the foregoing methyl derivative.

*Dimethylamidophenonaphthoxazone*,  $\overset{4}{\mathrm{O}}{:}\mathrm{C_{10}H_5}{<}\begin{matrix}\overset{1}{\mathrm{N}}\\ \underset{2}{\mathrm{O}}\end{matrix}{>}\mathrm{C_6H_3}\cdot\overset{4}{\mathrm{N}}\mathrm{Me_2}$, is obtained by adding nitrosodimethylmetamidophenol hydrochloride (40 grams) to a boiling solution of $\alpha$-naphthol (20 grams) in glacial acetic acid (200 grams); it melts at 244°, and crystallises from hot pyridine in large, green, lustrous prisms, which appear brownish-red in transmitted light. The dye is insoluble in water, but dissolves in common organic solvents, forming cherry-red solutions which exhibit scarlet fluorescence; the solutions in petroleum and benzene are yellowish-red, and exhibit green fluorescence. The *hydrochloride* crystallises in blue needles.

*Diethylamidophenonaphthoxazone* melts at 205°, and crystallises from hot pyridine in prisms which appear brownish-red by transmitted, green by reflected, light; the solutions of the dye in organic solvents resemble those of the foregoing methyl derivative. It dissolves in concentrated sulphuric acid with a reddish-brown coloration, which becomes blue on dilution, and the solution in concentrated hydrochloric acid is yellowish-brown, and yields a blue precipitate when diluted with water.

The absorption spectra of the foregoing dyes have been examined, and are collected in a diagram which appears in the original paper.

M. O. F.

**Action of Hypochlorous acid on Diazo-compounds.** By THEODOR ZINCKE (*Ber.*, 1895, **28**, 2948—2951).—Paradiazobenzenesulphonic acid can be oxidised with a solution of bleaching powder, the solutions being kept cool with ice, to an *acid*, $SO_3H{\cdot}C_6H_4{\cdot}N_2O_3H$; evidence of the formation of intermediate products was obtained. The acid crystallises in reddish-yellow needles, which explode feebly when heated; the *sodium*, with $H_2O$, *barium*, and *silver salts* are respectively brownish-red, yellowish-white, and brownish-yellow. The acid possibly has the constitution, $SO_3H{\cdot}C_6H_4{\cdot}N(OH){\cdot}NO_2$, but it is reduced by stannous chloride to Nietzki and Lerch's diamidobenzenesulphonic acid (Abstr., 1889, 144). C. F. B.

**New Base from Isobutylidenephenylhydrazine.** By KARL BRUNNER (*Monatsh.*, 1895, **16**, 849—865).—Whilst investigating the action of alcoholic zinc chloride on isobutylidenephenylhydrazine (compare Abstr., 1895, i, 475), the author has isolated a new base by means of its compound with zinc chloride $(C_{10}H_{11}N)_2,ZnCl_2 + \frac{1}{2}EtHO$. This crystallises in pale yellow, hexagonal plates, melts at 170—172°, dissolves readily in benzene, alcohol, and ether, and may be reprecipitated by the addition of light petroleum; it is decomposed by water, and, when heated, yields dimethylindole. The free base, $(C_{10}H_{11}N)_3$, is obtained by the addition of potassium hydroxide to a solution of the above-described compound with zinc chloride, and subsequent extraction with ether and recrystallisation from hot benzene. It dissolves in all ordinary organic solvents, and in mineral acids, and melts at 215—216°. The *picrate*, $C_{10}H_{11}N,C_6H_3N_3O_7$, is sparingly soluble in ether, but dissolves readily in alcohol and benzene, crystallises in rhombic scales, and melts at 134—135·5°. The *bromo*-derivative, $C_{10}H_9ONBr_2$, melts at 180—181°.

By the action of sodium amalgam on the base, another base of the formula $C_{10}H_{13}N$ or $C_{10}H_{11}N$ is obtained; this crystallises in long needles, melts at 79°, and forms a platinochloride, which melts and decomposes at 205°. G. T. M.

**Preparation of Ketones from Aromatic Propenyl ($\cdot CH{:}CHMe$) Derivatives.** By CARL HELL (*Ber.*, 1895, **28**, 2835—2838).—The compounds previously obtained from sodium ethoxide and isoeugenol ethyl and methyl ether dibromides (Abstr., 1895, i, 657) are not alcohols, $OH{\cdot}CR{:}CHMe$ or $CHR{:}CMe{\cdot}OH$, but ketones, $R{\cdot}CO{\cdot}CH_2Me$, as they readily yield *phenylhydrazones;* that from the *ethyl* ether melts at 86—87°, whilst the *methyl* derivative melts at 102—103°. By the action of bromine on the ketones, monobromoketones are formed. Anethoïl dibromide and bromanethoïl dibromide, by the action of chromic anhydride and glacial acetic acid, yield bromo-ketones, which are also formed when the products of the interaction of sodium ethoxide, anethoïl dibromide, and bromanethoïl dibromide respectively are brominated; these compounds are therefore $\alpha$-ketones. The conversion of an aromatic propenylic dibromide into an $\alpha$-ketone by means of sodium ethoxide takes place in four stages:

(1) $R{\cdot}CHBr{\cdot}CHBrMe = R{\cdot}CBr{:}CHMe + HBr$,
(2) $R{\cdot}CBr{:}CHMe + NaOEt = R{\cdot}C(OEt){:}CHMe + NaBr$,
(3) $R{\cdot}C(OEt){:}CHMe + H_2O = R{\cdot}C(OH){:}CHMe + EtOH$,
(4) $R{\cdot}C(OH){:}CHMe = R{\cdot}CO{\cdot}CH_2Me$. J. B. T.

**Etherification of Aromatic Acids.** By VICTOR MEYER (*Ber.*, 1895, **28**, 2773—2775).—In examining the constitution of aromatic acids by the etherification method, it is impossible to carry out the process in all cases at a low temperature, because some acids, which are only slightly soluble in alcoholic hydrogen chloride, do not undergo the reaction under these conditions. Moreover, the method of etherification by means of a current of hydrogen chloride passed into a boiling alcoholic solution cannot be generally used, because the characteristic differences in the behaviour of acids are often not shown when this process is employed. All simple acids, which do not contain more than two phenyl groups, behave in the characteristic way when they are boiled for 3—5 hours with alcohol containing 3 per cent. of hydrogen chloride (Fischer's method). More complex acids must be treated in solution in boiling alcohol with a current of hydrogen chloride. Several of the methyl derivatives of benzoic acid appear to behave in an exceptional manner, which is at present undergoing investigation. A. H.

**Diamidobenzoic acids.** By CARL HAEUSERMANN and H. TEICHMANN (*J. pr. Chem.*, 1895, [2], **52**, 428—429; compare Abstr., 1895, i, 531). —*Ethylic-2 : 5-diamidobenzoate* is prepared from ethylic 2 : 5-dinitrobenzoate in the manner already described (*loc. cit.*). It is a yellowish powder, melts at 50·5—51°, and dissolves somewhat easily in hot water, and very easily in alcohol and benzene. In dilute ethereal solution, it has a greenish fluorescence.

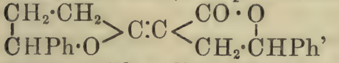
The *hydrochloride*, $C_6H_3(NH_2)_2{\cdot}COOEt,2HCl$, and *sulphate* are described. A. G. B.

**Products of the Reduction of Phenylbutyrolactone and Phenylparaconic acid.** By RUDOLPH FITTIG, ADOLF WOLFF, and JOHN SHIELDS (*Annalen*, 1895, **288**, 203—209).—When phenylbutyrolactone is reduced with hydriodic acid, phenylbutyric acid is formed; this substance melts at 51·7°, and not at 47·5°, as stated by Jayne. The calcium salt contains $3H_2O$, and crystallises from water in long needles; it undergoes no change at 120°. Sodium amalgam has but a slight action on a hot acid solution of phenylbutyrolactone; acetic acid and zinc dust give rise to a small proportion of phenylbutyric acid, 85 per cent. of the lactone employed being recovered unchanged. Tin and hydrochloric acid give rise to phenylbutyric acid, which is, for the most part, converted into the ethylic salt, the reaction being studied in alcoholic solution; 37 per cent. of the lactone remains unaltered.

Hydriodic acid converts phenylparaconic acid into benzylsuccinic acid, phenylbutyric acid being also formed as a secondary product.

M. O. F.

**Action of Sodium Ethoxide on Phenylbutyrolactone.** By Rudolph Fittig, Adolf Wolff, and Rudolph Lesser (*Annalen*, 1895, **288**, 192—202; compare Abstr., 1892, 813).—*Diphenyldibutyrolactone.*



$$\begin{matrix}CH_2\cdot CH_2\\ | \\ CHPh\cdot O\end{matrix}\!\!>C:C<\!\!\begin{matrix}CO\cdot O\\ \quad\ \ | \\ CH_2\cdot CHPh\end{matrix},$$

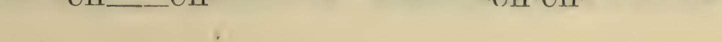
is obtained by heating phenylbutyrolactone with sodium ethoxide and alcohol for 15—18 hours in a reflux apparatus; it crystallises from alcohol in rosettes of colourless needles, and melts at 83—84°. The substance is unsaturated, and gives rise to three distinct compounds on treatment with bromine in carbon bisulphide solution; they melt at 109°, 150—151°, and 117—118° respectively.

*Diphenyloxetonecarboxylic acid*, $C_{20}H_{20}O_4$, is obtained by heating the dilactone with aqueous sodium hydroxide and some alcohol; it decomposes at 147—148°. The *barium* salt decomposes above 100°, the *calcium* salt is anhydrous, and the *silver* salt becomes only slightly coloured on exposure to light.

*Diphenyloxetone*, $C_{19}H_{20}O_2$, is produced on heating the foregoing acid with dilute hydrochloric acid in a reflux apparatus, and is also slowly formed when water alone is used; it is a neutral oil, which undergoes slight decomposition when heated. Diphenyloxetone dissolves readily in organic solvents, with the exception of petroleum, which precipitates it completely from the solution in benzene; it does not reduce an ammoniacal silver solution, and yields no solid derivative with sodium hydrogen sulphite.

M. O. F.

**Action of Ethylic Iodide on Potassium β-Resorcylate.** By Georg Gregor (*Monatsh.*, 1895, **16**, 881—892).—*Ethoxy-β-resorcylic acid*, $C_7H_5O_3\cdot OEt$, is formed, together with several neutral substances, by the action of ethylic iodide on potassium β-resorcylate in alcoholic solution. It crystallises in white needles, melts at 154°, and is sparingly soluble in cold water, but dissolves more readily in hot water, alcohol, ether, and benzene. The *sodium salt*, $C_9H_9NaO_4 + H_2O$, crystallises in scales; the *barium salt* is anhydrous, and crystallises in small needles; the *silver salt* contains $10H_2O$; the *lead salt*, $(C_9H_9O_4)_2Pb + 8H_2O$, and other salts are also described. From the behaviour of the ethylic salt towards dilute potassium hydroxide solution, the author concludes that the formula is



$$CO<\begin{matrix}CH_2\cdot C(OEt)\\ CH{=\!=}CH\end{matrix}\gg C\cdot COOH \quad \text{or} \quad OEt\cdot C\ll\begin{matrix}CH_2\cdot CO\\ CH\cdot CH\end{matrix}\gg C\cdot COOH,$$

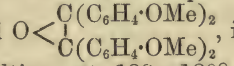
being derived from the secondary tertiary form, and not from the bi-tertiary form of resorcinol. He also suggests that the acid formed by the action of ethylic iodide on potassium-β-resorcylate perhaps consists of two isomeric acids, which are not easily separated (compare Tiemann and Parrisius, Abstr., 1881, 271). G. T. M.

**Halogen Derivatives of the Sulphonamides.** By J. H. KASTLE (*Amer. Chem. J.*, 1895, **17**, 704—708).—Dichlorobenzenesulphonamide is readily prepared by dissolving benzenesulphonamide in the smallest quantity of soda (1 : 10), a rapid current of chlorine is passed through the solution, and the first portion of precipitate, which contains much unchanged sulphonamide, is removed, the filtrate treated with chlorine, the crude product washed with hot water by decantation, dissolved in alcohol, and precipitated by the addition of water. It is extremely stable. When heated at about 170°, it is resolved into chlorine, nitrogen, hydrogen chloride, and benzenesulphonic chloride, the latter being produced in almost theoretical quantity. By the action of bromine water on parachlorobenzenesulphonamide in soda solution, a yellow crystalline *dibromide* is formed. J. B. T.

**Formation of Indigo in Plants of the Order Indigofera.** By C. J. VAN LOOKEREN and P. J. VAN DER VEEN (*Landw. Versuchs. Stat.*, 1895, **46**, 249—258).—See this vol., ii, 207.

**Coloured Aromatic Thioketones.** By LUDWIG GATTERMANN (*Ber.*, 1895, **28**, 2869—2877).—*Paradimethoxythiobenzophenone*, $CS(C_6H_4{\cdot}OMe)_2$, is prepared by the interaction of anisoïl, thiocarbonyl chloride, and aluminium chloride, and crystallises from alcohol in long, dark blue needles melting at 115°. Solutions of the ketone are of a bluish-violet colour; its constitution is shown by its conversion into dimethoxybenzophenone [CO : OMe = 1 : 4] when treated with alcoholic potash. Attempts to prepare derivatives of the thio-ketone were unsuccessful on account of the readiness with which the sulphur is eliminated.

*Paradiethoxythiobenzophenone*, $CS(C_6H_4{\cdot}OEt)_2$, prepared in a similar manner from phenetoïl, crystallises in sky blue plates, melts at 118—119°, and, with alcoholic potash, is converted into paradiethoxybenzophenone. The molecular weight was determined by the cryoscopic method in naphthalene solution. *Paradipropoxythiobenzophenone*, $CS(C_6H_4{\cdot}OPr^a)_2$, from propoxybenzene, crystallises in blue plates and melts at 105—106°. *Paradipropoxybenzophenone*, $CO(C_6H_4{\cdot}OPr^a)_2$, formed by the action of alcoholic potash on the preceding compound, crystallises in colourless plates, and melts at 127°. The *oxime* is deposited in colourless needles melting at 113°. *Diethoxydimethylthiobenzophenone*, $CS(C_6H_3Me{\cdot}OEt)_2$ [Me : OEt = 1 : 2], prepared from orthoethoxymethylbenzene, melts at 117—118°, and gives a violet solution in alcohol, from which it is deposited in olive-green needles with a steel-blue reflex; from light petroleum it crystallises in elongated steel-blue crystals. *Diethoxydimethylbenzophenone*, $CO(C_6H_3Me{\cdot}OEt)_2$ [Me : OEt = 1 : 2], crystallises in colourless, silky, lustrous needles melting at 105—106°. *Dimethoxydimethylthiobenzophenone*, $CS(C_6H_3Me{\cdot}OMe)_2$ [$Me : OMe = 1 : 2$], could not be completely separated from the ketone, with which it appears to crystallise; the long, steel-blue needles obtained from its solution in light petroleum, dissolve with a violet coloration, and melt at 114°. *Dichlorodimethoxythiobenzophenone*, $CS(C_6H_3Cl{\cdot}OMe)_2$ [$Cl : OMe = 1 : 2$], from orthochloranisoïl, crystallises in moss-green needles, melts at 178—179°, and dissolves with a violet colour. The *ketone*, $CO(C_6H_3Cl{\cdot}OMe)_2$, crystallises in colourless needles, and melts at 183—184°. *Dichlorodiethoxythiobenzophenone*, $CS(C_6H_3Cl{\cdot}OEt)_2$ [$Cl : OEt = 1 : 2$], crystallises in dark green needles, melts at 141—142°, and yields blue-violet solutions. The *ketone*, $CO(C_6H_3Cl{\cdot}OEt)_2$, crystallises in colourless needles, and melts at 122—123°. *Dibromodimethoxythiobenzophenone*, $CS(C_6H_3Br{\cdot}OMe)_2$ [$Br : OMe = 1 : 2$], from orthobromanisoïl, dissolves in alcohol with a violet colour, and crystallises with difficulty in dark green needles melting at 189—190°. The *ketone*, $CO(C_6H_3Br{\cdot}OMe)_2$, crystallises in colourless needles melting at 180—181°.

The preceding thioketones, when heated at 200—220° with finely divided copper, in an atmosphere of carbonic anhydride, yield cupric sulphide and derivatives of tetraphenylethylene. *Tetramethoxytetraphenylethylene*, $C_2(C_6H_4{\cdot}OMe)_4$, from paradimethoxythiobenzophenone, crystallises from glacial acetic acid in colourless needles with a pale blue fluorescence, melts at 181—182°, and, in presence of bromine vapour or lead peroxide, yields a blue compound which has not yet been isolated. By the further action of lead peroxide at the ordinary temperature, the compound  $O<\begin{matrix}C(C_6H_4{\cdot}OMe)_2\\ |\\ C(C_6H_4{\cdot}OMe)_2\end{matrix}$, is obtained, it forms long, colourless crystals melting at 188—189°. *Tetrethoxytetraphenylethylene*, $C_2(C_6H_4OEt)_4$, resembles the methoxy-derivative, crystallises in long needles with an intense green fluorescence, melts at 120—121°, and, when reduced with sodium in alcoholic solution, yields *tetrethoxytetraphenylethane*, $C_2H_2(C_6H_4{\cdot}OEt)_4$, which crystallises in colourless needles melting at 163—164°. *Tetrapropoxytetraphenylethylene*, $C_2(C_6H_4{\cdot}OPr^{\alpha})_4$, from dipropoxythiobenzophenone, crystallises in green, fluorescent needles, melts at 139—140°, and becomes blue when oxidised. *Tetramethoxytetramethyltetraphenylethylene*,

$$C_2(C_6H_3Me{\cdot}OMe)_4\ [Me : OMe = 1 : 2],$$

crystallises in fluorescent needles melting at 195°; the corresponding *ethoxy-derivative*, $C_2(C_6H_3Me{\cdot}OEt)_4$, is deposited from a mixture of pyridine and alcohol in green, fluorescent plates melting at 214°; both compounds become blue when oxidised. *Tetrachlorotetramethoxytetraphenylethylene*, $C_2(C_6H_3Cl{\cdot}OMe)_4$ [$Cl : OMe = 1 : 2$], crystallises from glacial acetic acid in colourless needles melting at 257°. The *ethoxy-derivative*, $C_2(C_6H_3Cl{\cdot}OEt)_4$, is deposited from benzene in colourless, feathery crystals melting at 258—259°. Neither of these compounds becomes blue when oxidised. The compound, $C_2(C_6H_4{\cdot}NMe_2)_4$, is prepared by the action of copper on the corresponding thioketone and crystallises from acetone, on the addition of alcohol, in greenish-yellow needles, from benzene in highly lustrous prisms, melting at

310—315°. It is a strong base, which dissolves readily in dilute acids, and, on adding lead peroxide to its acetic acid solution, gives a dull, unstable violet coloration.

Bergreen prepared a reddish-brown oil by the interaction of benzene, thiocarbonyl chloride, and aluminium chloride; this experiment has been repeated, but a blue, oily liquid, consisting of a mixture of ketone and thioketone was obtained; these could not be separated. Other attempts to prepare thiobenzophenone by the action of hydrogen sulphide on benzophenoneanilide, to which a little hydrogen chloride had been added, and by the interaction of phosphorus pentasulphide in benzene solution, and benzophenone, were also unsuccessful; the latter method gave a product containing 50 per cent. of the thioketone, as shown by the production of tetraphenylethylene, which is not formed by heating copper with benzophenone. The colour of the above thioketones, and also that of thiacetophenone, shows that the group CS is a chromophore.

J. B. T.

**Hydrazones of Fluorenone and its Derivatives.** By GUIDO GOLDSCHMIEDT and FRANZ SCHRANZHOFER (*Monatsh.*, 1895, **16**, 807—827).—The *phenylhydrazone* of fluorenone (diorthodiphenylene ketone) is obtained when an alcoholic solution of fluorenone is heated in a water bath with a slight excess of phenylhydrazine, and the product is subsequently acidified with acetic acid. On cooling, the compound separates in beautiful, yellow needles, and these, when recrystallised from alcohol form long prisms which melt at 151—151·5°.

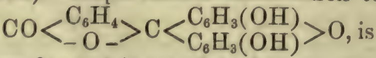
When dry chlorine is led into a solution of the ketone in chloroform, the following two well characterised chlorinated derivatives are obtained:—*Chlorofluorenone* crystallises from dilute alcohol in long, yellow needles, melts at 115°, and forms a *phenylhydrazone* which melts at 139—141°. *β-Dichlorofluorenone* crystallises from alcohol in beautiful, long, yellow needles, melts at 188—189° (compare Hodgkinson and Matthews, Trans., 1883, 165), and forms a *phenylhydrazone*,

$$C_{13}H_6Cl_2N_2HPh,$$

which crystallises in yellow needles, and melts at 185—186°. *β-Dibromofluorenonephenylhydrazone* melts at 190°. *δ-Dibromofluorenone* melts at 262°, is yellow, and forms a *phenylhydrazone* melting at 252°. *Nitrofluorenonephenylhydrazone* melts at 210—214°. *α-Dinitrofluorenonephenylhydrazone* melts at 257—258°. *β-Dinitrofluorenone* forms yellow needles, melts at 220°, and yields a *phenylhydrazone* melting at 227—228°,

The results obtained in this investigation, taken in conjunction with the fact that ellagic acid, a fluorenone derivative, does not yield a hydrazone, have not thrown light on the formation of hydrazones, as expected by the authors.

G. T. M.

**The Phthaleïn Groups.** By RICHARD MEYER and HEINRICH MEYER (*Ber.*, 1895, **28**, 2959—2964).—Experiments undertaken to ascertain whether quinolphthaleïn,  $CO<{}^{C_6H_4}_{-O-}>C<{}^{C_6H_3(OH)}_{C_6H_3(OH)}>O$, is related to fluoran, gave a negative result, and it was found impossible to decide as to the structure of this substance. When it is heated with strong aqueous ammonia, it yields a colourless *imido-compound*, an imido-group having been substituted for one of the oxygen atoms; this compound decomposes above 310° without melting. The phthaleïn further yields a colourless *dibenzoate* melting at 252—253°. C. F. B.

**Substitution Products of the Carbonates and Phosphates of α-Naphthol and β-Naphthol: Preparation of 1 : 4-Chloronaphthol and 1 : 4-Bromonaphthol.** By Frédéric Reverdin and Hugo Kauffmann (*Ber.*, 1895, **28**, 3049—3058; compare Abstr., 1895, i, 151).—4-*Nitro-α-naphthylic carbonate*, $(NO_2\cdot C_{10}H_6\cdot O)_2CO$, is obtained by the action of nitric acid on α-naphthylic carbonate dissolved in glacial acetic acid; according to the quantity of the diluent employed, it is obtained in a form which crystallises from benzene in pale yellow needles melting at 148°, or as the modification separating in yellowish needles which melt at 212°. Both substances yield 1 : 4-nitronaphthol when hydrolysed with alcoholic potash, and in the case of the modification melting at 148°, α-naphthol is produced at the same time.

The *dichloride* of α-naphthylic carbonate $(C_{10}H_7Cl_2O)_2CO$, is formed when chlorine is led into a cold solution of α-naphthylic carbonate in benzene or carbon tetrachloride; it crystallises in white needles, which melt and decompose at 200°. 4-*Chloro-α-naphthylic carbonate* is produced when this substance is distilled or treated in chloroform solution with bases or acetic anhydride; it is also obtained by passing chlorine into a hot solution of α-naphthylic carbonate in glacial acetic acid or a cold solution of this substance in carbon tetrachloride containing 5 per cent. of antimony trichloride. The compound is sparingly soluble in most solvents, and crystallises from benzene in white needles, which melt at 228°.

1 : 4-*Chloronaphthol* is obtained by hydrolysing chloro-α-naphthylic carbonate with alcoholic potash; at 100° it sublimes in long, white needles, melting at 116°, and is readily soluble in organic solvents. A blue precipitate is formed when bleaching powder or ferric chloride is added to the neutral aqueous solution, and its behaviour in alkaline solution towards chloroform, carbon tetrachloride, and formaldehyde, resembles that of naphthol; it reacts with sodium nitrite and hydrochloric acid, and yields dyes with diazo-compounds. The *acetyl* derivative melts at 44°, and the *picrate* at 171°. 1 : 4-Chloronaphthol develops a blue coloration with dimethylparaphenylenediamine; 1 : 2 : 4-dichloronaphthol is produced when chlorine is passed into the solution in glacial acetic acid.

4-*Bromo-α-naphthylic carbonate* crystallises from benzene and melts at 214°. When hydrolysed with alcoholic potash, it yields 1 : 4-*bromonaphthol*, which melts at 127—128°, and yields a *picrate* and an *acetyl* derivative which melt at 167° and 51° respectively; 1 : 4-bromonaphthol has also been obtained by the action of boiling water on diazotised 1 : 4-bromonaphthylamine, and when treated with bromine in glacial acetic acid solution it yields 1 : 2 : 4-dibromonaphthol, which melts at 105·5°.

The behaviour of α-naphthylic phosphate (m. p. 149—150°) closely resembles that of α-naphthylic carbonate, and the substance yields a sulphonic acid, the sodium salt of which, on hydrolysis, yields 1 : 4-naphtholsulphonic acid and sulphonaphthylphosphinate.

1-*Bromo-β-naphthylic carbonate* is obtained by the action of phosgene on an alkaline solution of 1 : 2-bromonaphthol; it crystallises from ethylic acetate in white needles, and melts at 188—189°. 1-*Iodo-β-naphthylic carbonate* crystallises in white needles, which become yellow on exposure to air, and melt at 188—189°.

M. O. F.

**Paranthracene or Dianthracene. A Polymeric Modification of Anthracene.** By William R. Orndorff and F. K. Cameron (*Amer. Chem. J.*, 1895, **17**, 658—681).—The paranthracene was prepared by the action of sunlight on anthracene suspended in benzene and xylene; the operation is expedited by shaking occasionally to remove deposited material from the glass. The product was purified by extraction with alcohol, ethylic acetate, and benzene, and the residue crystallised repeatedly from benzene in an extraction apparatus. Dimethylaniline is unsuitable as a solvent. Paranthracene crystallises in thin plates, which are fully described, belonging to the ortho-rhombic system $a : b : c = 0·6762 : 1 : 1·5731$; it melts at 242—244°, being quantitatively converted into anthracene; the same change takes place by prolonged heating alone at 230—235°, or in boiling naphthalene (218°), and partially in boiling dimethylaniline (192°), and in aniline (182°). The compound does not fluoresce either in solution or in the solid state. The sp. gr. = 1·265 at 27°/4°, and that of anthracene = 1·250; the following numbers express the solubility of paranthracene in the solvents (100 parts) at their respective boiling points: ethylenic bromide, 0·2273; pyridine, 1·106: anisoïl, 1·46; phenetoïl, 1·5. The molecular weight was determined by the boiling point method in the above solvents; the values are, in ethylenic bromide, 179—346, average of 10 determinations, 285; in pyridine, 317—387, average of 9 determinations, 354; in anisoïl, 331—397, average of 13 determinations, 362; in phenetoïl, 329—396, average of 8 determinations, 355. Elb's conclusion that the molecular weight of paranthracene is twice that of anthracene is thus confirmed, and it is suggested that this should be expressed by the name *dianthracene*.

Attempts to prepare paranthracene by dropping a little of it into melted anthracene at 215—240°: by the action on it of hydrogen chloride, either aqueous or alcoholic, at 220°; by treatment of anthracene dibromide with zinc dust; by heating anthracene with sodium amalgam and alcohol, or with sodium and benzene, were all unsuccessful. Anthraquinone, dihydroanthracene, dichloranthracene, phenanthrene, retene, camphor, and phenylacridine were unchanged after exposure to light during several weeks; anthranol, in benzene solution, under these conditions, yielded an almost colourless product, which becomes brown and melts at 265—270°; it is insoluble in boiling alkali and less soluble in other media than anthranol. Acridine, in solution, when exposed to sunlight, gave a pale yellow, crystalline compound, which could not be dissolved, and which does not form salts with acids; when rapidly heated, it melts at 276°, when slowly heated it volatilises, without melting, at 250°, and, in both cases, is converted into acridine; the same change is produced by prolonged boiling in various liquids. Graebe and Liebermann's formula is accepted for anthracene, with the modification that if von Baeyer's centric formula is adopted for benzene and its carboxylic acids, the benzene nuclei in anthracene must, from its synthetical formation, be represented in the same manner; the stability of anthraquinone and dihydroanthracene towards oxidising and reducing agents respectively is in accord with this. The difference in behaviour of anthracene and phenanthracene support the view that the former contains two benzene nuclei and two $\gamma$-carbon atoms (paraffinoïd residue), and that the latter contains three benzene nuclei. With the above modifications, Linebarger's formula for paranthracene is accepted; its formation is ascribed to the tendency to form rings of six members, the para-linkage of the $\gamma$-carbon atoms being resolved. J. B. T.

**Limonene and its Derivatives.** By EDWARD KREMERS (*Amer. Chem. J.*, 1895, **17**, 692—697).—The limonene employed boiled at 174·5—175°, and was prepared by the fractionation of commercial "carvene"; $[\alpha]_D = +120{\cdot}466°$, whilst the value given by Wallach and Conradi is 106·8°. The specific rotatory power of limonene solutions of varying content, in ordinary and absolute alcohol, chloroform, and glacial acetic acid, was determined; in the case of absolute alcohol and chloroform, the rotatory power decreases with fair regularity as the proportion of solvent rises. For solutions containing 10, 50, and 90 per cent. $[\alpha]_D = 113{\cdot}430°$ and 115·673°; 115·690° and 117·604°; 118·036° and 118·733° respectively. The fractions boiling at 172·5—177° have all a lower refractive power than limonene except the one boiling at 174—174·5°, for which $[\alpha]_D = 120{\cdot}672°$. Limonene hydrochloride, when treated with water in a sealed tube at the ordinary temperature, is slowly converted into terpene hydrate, which, when heated above its melting point, is resolved into terpene. When exposed to air, the oily mother liquid darkens, and the crystals gradually dissolve in it. J. B. T.

**Nitration of Menthone.** By MICHAEL I. KONOVALOFF (*Compt. rend.*, 1895, **121**, 652—653).—Nitric acid of sp. gr. 1·075 acts very readily on menthone, $C_{10}H_{18}O$, in sealed tubes at 100°, and yields nitromenthone, $NO_2{\cdot}C_{10}H_{17}O$, a yellowish liquid with an odour recalling that of menthone. It boils and slightly decomposes at 135—140° under a pressure of 15 mm.; sp. gr. = 1·0856 at 0° and 1·0591 at 20°. It is insoluble in water, concentrated hydrochloric acid, and sodium carbonate solution, and only slightly soluble in concentrated aqueous potash. With sodium ethoxide in presence of alcohol, nitromenthone yields a salt which, when decomposed by sulphuric acid, gives a liquid acid of the composition $C_{10}H_{19}NO_4$. It boils and slightly decomposes at 190—195° under a pressure of 13 mm., and dissolves readily in sodium carbonate solution, but not in water or hydrochloric acid.

When reduced, nitromenthone yields a basic compound, and it seems to have the constitution

$$[CPr{\cdot}NO_2 : CO : CH_2 : CHMe : CH_2 : CH_2 = 1:2:3:4:5:6],$$

the constitution of the nitro-acid being

$$CHMe_2{\cdot}CH(NO_2){\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}COOH.$$

C. H. B.

**Action of Silver Oxide on Dibromomenthylamine. Menthylhydrazine.** By NIC. KIJNER (*J. pr. Chem.*, 1895, [2], **52**, 424—426).—*Menthonementhylhydrazone*, $C_{10}H_{19}N{\cdot}N{:}C_{10}H_{18}$, is produced by adding moist silver oxide to dibromomenthylamine, warming at 50—60°, and extracting with ether. It crystallises in long, greenish-yellow needles, and melts at 92—93°. It is lævorotatory in solution ($[\alpha]_D = -366{\cdot}5°$). Boiling dilute hydrochloric acid converts it into menthone and *menthylhydrazine hydrochloride*, $C_{10}H_{19}N_2H_3Cl$, which dissolves in water, alcohol, and ether, and is lævorotatory ($[\alpha]_D = -46{\cdot}05°$). *Menthylhydrazine* is a liquid which boils at 235—240°, and by oxidation yields *menthane*, $C_{10}H_{20}$, which boils between 165—169°. A. G. B.

**Action of Hydroxylamine on *l*-Dibromomenthylamine.** By NIC. KIJNER (*J. pr. Chem.*, 1895, [2], **52**, 426—427).—The author has published (*J. Russ. Chem. Soc.*, 1894, **26**, ii, 132) the result of the reaction between hydroxylamine hydrochloride and dibromomenthylamine. The change occurs in the sense of the equation $C_{10}H_{19}{\cdot}NBr_2 + NH_2{\cdot}OH = C_{10}H_{19}Br + N_2 + H_2O + HBr$.

It is pointed out that this reaction is analogous to that between hydroxylamine and dichloromethylamine, to which attention has just been called by Bamberger and Renauld (Abstr., 1895, i, 494).

A. G. B.

**Partial Synthesis of Camphor: Constitution of Camphoric acid and Camphorone.** By JULIUS BREDT and M. VON ROSENBERG (*Annalen*, 1895, **289**, 1—14).—*Homocamphoric acid* is the name by which the authors refer to hydroxycamphocarboxylic acid, $C_{11}H_{18}O_4$, obtained by Haller (*Dissertation, Nancy*, 1879, 29) on hydrolysing cyanocamphor with aqueous caustic potash; the *silver* salt is a white powder dissolving with difficulty in water, and the calcium salt contains $7H_2O$, which is lost at 140°.

When the dry calcium salt of homocamphoric acid is distilled in an atmosphere of carbonic anhydride, camphor is produced in quantity amounting to 70 per cent. of the theoretical yield; camphor obtained in this way is in every respect identical with ordinary dextro-camphor.

The authors discuss the constitution of camphoric acid and camphorone. M. O. F.

**Tiemann's Formulæ for Camphor and Campholenic acid.** By JULIUS BREDT (*Annalen*, 1895, **289**, 15—19).—The author draws attention to the identity of his expression for the constitution of camphor (Abstr., 1894, i, 141) with the formula advocated by Tiemann (Abstr., 1895, i, 426 and 675). M. O. F.

**Etherification and Hydrolysis.** By JULIUS W. BRÜHL (*Ber.*, 1895, **28**, 2868—2869).—A question of priority with Wegscheider (this vol., i, 95) as to the discovery of the fact that, by the action of

hydrogen chloride and alcohol, the carboxyl group which is most readily etherified is subsequently also the most easily hydrolysed; this was shown three years ago by the author in the case of camphoric acid.
J. B. T.

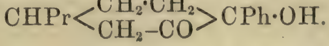
**Acids formed by Oxidation of inactive Campholenic acid.** By AUGUSTE BÉHAL (*Compt. rend.*, 1895, **121**, 465—468).—The acid, $C_6H_{10}O_4$, obtained by the action of nitric acid on inactive campholenic acid (this vol., i, 55) is identical with the unsymmetrical dimethylsuccinic acid, $COOH{\cdot}CMe_2{\cdot}CH_2{\cdot}COOH$, obtained by the interaction of ethylic bromisobutyrate and ethylic sodiomalonate. It melts at 143—144°; its anhydride melts at 22°, and yields with aniline an anilide melting at 185°, whilst the corresponding imide, obtained by the action of heat, melts at 86°.

It would seem to follow that the acid $C_7H_{12}O_4$ (*loc. cit.*) is a trimethylsuccinic acid or one of the dimethylglutaric acids, in which the two methyl groups are attached to the same carbon atom. The behaviour of hydroxycamphoronic acid on heating indicates that it probably has the constitution $COOH{\cdot}CMe_2{\cdot}CH(CH_2{\cdot}COOH)_2$.
C. H. B.

**Synthesis of a New Ketonic acid.** By E. BURKER (*Compt. rend.*, 1895, **121**, 607—610).—The action of camphoric anhydride on benzene in presence of aluminium chloride, if the temperature is not allowed to rise too high, yields an *acid* which, when purified, has the composition $C_{15}H_{20}O_2$, and forms small, nacreous, white crystals melting at 135—137°, and boiling at 320° under a pressure of 760 mm., or at 250° in a vacuum. Its molecular weight in solution in benzene is 232. It is almost insoluble in water, and very slightly in light petroleum, but dissolves readily in other organic solvents.

The alkali salts crystallise, and are decomposed by carbonic anhydride. The barium salt forms small, white, nacreous crystals containing $9H_2O$.

The *ethylic* salt, $C_{15}H_{19}O_2Et$, dissolves very readily in light petroleum, from which it separates in large monoclinic crystals. The *methylic* salt also crystallises from light petroleum in long monoclinic needles, which melt at 85—86°. Both are decomposed at once by sulphuric acid, but are very slowly attacked by alkalis. The *anhydride* is readily obtained by the action of acetic anhydride, but not by the action of acetic chloride; it forms small, white crystals which melt at about 135°, and are only slowly attacked by alcoholic potash. The *amide* forms long, silky, white needles which melt at 77°, and dissolve in boiling water; it is very slowly attacked by alcoholic potash. The *phenylhydrazide* forms long needles which melt at 156°.

The formation of this compound is readily explained by Friedel's formula for camphoric acid, but not by any formula which assumes the presence of two COOH groups. Its constitution is therefore represented as  $CHPr{<}\substack{CH_2{\cdot}CH_2\\CH_2{-}CO}{>}CPh{\cdot}OH$.
C. H. B.

**Digitalin ("Digitalinum Verum").** By HEINRICH KILIANI (*Arch. Pharm.*, 1895, **233**, 698—699).—The author has succeeded in obtaining digitalin in a crystalline form by dissolving one part of the pure glucoside in two parts of boiling 85 per cent. methylic alcohol. The temperature of the solution is then allowed to fall gradually to 45°, at which point it is maintained; the substance is deposited in the form of white needles, in part aggregated to nodular masses. From a more dilute solution (1 in 10), the temperature of which is allowed to fall from the boiling point to the ordinary temperature, a small quantity of the substance is deposited wholly in the form of stellar aggregates of needles. A. L.

**Root of Aristolochia Argentina.** By OSWALD HESSE (*Arch. Pharm.*, 1895, **233**, 664—697).—On account of its acid properties, the name *aristolochic acid* is suggested for Pohl's "aristolochine" (Abstr., 1892, 874), the latter name being reserved for the alkaloïd obtained from *Aristolochia argentina.* The author has obtained from the root of this plant a starch-like substance, a resin, an ethereal oil of high boiling point, palmitylphytosterin, $C_{42}H_{74}O_2$, aristolin, $C_{15}H_{28}O_3$, the isomeric aristinic and aristidinic acids, $C_{18}H_{13}NO_7$, aristolic acid, $C_{15}H_{11}NO_7$ or $C_{15}H_{13}NO_7$, and the alkaloïd aristolochine (compare Abstr., 1892, 894).

The ethereal extract of the root is saturated with gaseous ammonia, and filtered from the resulting precipitate. The filtrate is neutralised, separated from ammonium and aristolochine salts, and evaporated. The residual, oily mass partially crystallises, the liquid portion on distillation yielding a colourless, highly refractive oil, having a disagreeable odour. Light petroleum separates the crystalline mass into soluble palmitylphytosterin and an insoluble substance—*aristolin*, $C_{15}H_{28}O_3$, probably an alcohol; it crystallises from alcohol in spherical aggregates of minute needles, and dissolves readily in ether and in hot alcohol. It melts and decomposes at 265°.

The precipitate produced by ammonia consists of a mixture of the ammonium salts of aristinic, aristidinic, and aristolic acids, of which the first-named preponderates, and may be separated by means of its potassium salt, which is precipitated from solution on adding a slight excess of alkali. *Aristinic acid*, $C_{18}H_{13}NO_7$, crystallises from acetic acid in greenish-yellow leaflets or needles which melt and decompose at about 275°, at higher temperatures evolving yellowish vapours which condense to form a yellow sublimate. When it is fused with potash, ammonia is evolved. It forms two series of salts, a normal and a basic; the former alone have been obtained in a crystalline form. The *potassium* salt, $C_{18}H_{12}NO_7K,2H_2O$, forms small red crystals, but when anhydrous is yellow. The *sodium* salt resembles that of potassium. The *ammonium* salt crystallises in red needles. The *barium*, $(C_{18}H_{12}NO_7)_2Ba + 2H_2O$, *calcium*, $(C_{18}H_{12}NO_7)_2Ca + 4H_2O$, *copper*, $(C_{18}H_{12}NO_7)_2Cu + 3H_2O$, *lead*, $(C_{18}H_{12}NO_7)_2Pb + 2H_2O$, and *silver* salts, $C_{18}H_{12}NO_7Ag$, crystallise in small, orange needles. The *methylic* salt, $C_{18}H_{12}NO_7Me$, forms yellow needles, and melts at about 250°.

The potassium salt of aristidinic acid is separated from that of aristolic acid by adding to the solution a large excess of potash, in which the former salt is insoluble. *Aristidinic acid*, $C_{18}H_{13}NO_7$, is soluble in acetic acid and in alcohol; it forms small, greenish-yellow crystals which darken at 230°, and melt at 260°. *Aristolic acid*, $C_{15}H_{11}NO_7$ or $C_{15}H_{13}NO_7$, is readily soluble in ether, acetic acid, and hot alcohol, and crystallises from the latter in small, orange-red needles, which darken at 223°, and melt at 260—270°. These three acids and aristolochic acid dissolve in warm sulphuric acid, forming beautiful dark green solutions; this appears to indicate that these substances are closely allied in constitution. It is possible that aristolochic acid is the next higher homologue of aristinic acid, and that aristidinic acid is methylaristolochic acid. The latter view is supported by the circumstance that aristidinic acid appears to contain a methoxyl group. A. L.

**Chlorophyll.** By EDWARD SCHUNCK and LEO MARCHLEWSKI (*Annalen*, 1895, **288**, 209—218; compare Abstr., 1894, i, 341, and 1895, i, 296).—The authors, having already established analytically the composition of phyllotaonin (*loc. cit.*), confirm the expression, $C_{40}H_{40}N_6O_6$, by ebullioscopic determinations of the molecular weight. Phyllotaonin is indifferent towards hydroxylamine, and has no reducing action on Fehling's solution or an ammoniacal solution of silver; this behaviour indicates that phyllotaonin and chlorophyll are not aldehydic in character. Owing to the opacity of dilute solutions containing ethylphyllotaonin, it is not possible to determine whether this substance is optically active; the authors consider, however, that this is probably the case, because phyllotaonin forms monosymmetric crystals which exhibit hemihedral faces.

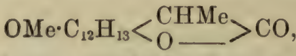
When ethylphyllotaonin is distilled from zinc dust, a small quantity of an oil is produced which becomes brown on exposure to the atmosphere, and yields a red powder when treated with hot, dilute hydrochloric acid; moreover, the vapour which is evolved by phyllotaonin, when heated in a dry tube, produces an intense red stain on a fir splinter which has been moistened with hydrochloric acid. These facts are recognised as indicating relationship between chlorophyll and pyrroline; Nencki and Sieber have recorded a similar observation in connection with hæmatoporphyrin.

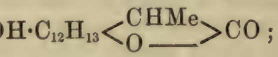
The remaining portion of the paper is devoted to criticism of Étard's investigation of lucern (Abstr., 1895, i, 389), the results of which the authors regard as erroneous. M. O. F.

**The Yellow Colouring Matter of Autumn Leaves.** By GEORG STAATS (*Ber.*, 1895, **28**, 2807—2809).—The yellow colouring matter which may be extracted from autumnal leaves by boiling alcohol is not identical with phylloxanthin, and is called by the author *autumnixanthin*. From whatever source the yellow colouring matter is derived, its alcoholic solution gives, with potash, a reddish-brown precipitate, which dissolves in water or acids. The potassium compound has been obtained in minute crystals, but has not been analysed. The autumnixanthine itself has not been obtained crystalline. When its alcoholic solution is slowly added to boiling hydrochloric acid, a red solution is formed. A. H.

**Pelageïne.** By Arthur B. Griffiths and C. Platt (*Compt. rend.*, 1895, **121**, 451—452).—The violet pigment of the medusa dissolves with the fats in alcohol and ether. The filtered solution is evaporated to dryness, treated with sodium hydroxide, and the pigment extracted with carbon bisulphide. It is an amorphous product of the composition $C_{20}H_{17}NO_7$, insoluble in water, soluble in alcohol, ether, and ethylic acetate, and very soluble in carbon bisulphide. The solutions show no characteristic absorption bands. When exposed to light, the pigment is decolorised. C. H. B.

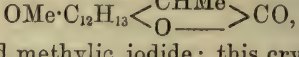
**The Four Santonous acids.** By Americo Andreocci (*Gazzetta*, 1895, **25**, i, 452—568).—In alcoholic solution, santonin has the specific rotation $[\alpha]_D = -173$, the rotation increasing to $-176{\cdot}5$ in 80 per cent. alcohol, whilst when dissolved in 38 per cent. hydrochloric acid or hydrobromic acid (sp. gr. 1·38), the value of $[\alpha]_D$ becomes $-340$ and $-345$ respectively, although the santonin is precipitated unchanged by addition of water; the increase in rotation is probably due to the conversion of the ketonic group into a $:C(OH)X$ group, by addition of water or of the halogen hydride. The behaviour of santonic acid is similar; in 100 and 50 per cent. alcohol it has the specific rotations $[\alpha]_D = -42{\cdot}1$ and $-74{\cdot}1$ respectively, and in 9·5 and 38 per cent. hydrochloric acid $[\alpha]_D = -87{\cdot}9$ and $-138{\cdot}6$ respectively.

*Methyldesmotroposantonin*,  $\mathrm{OMe{\cdot}C_{12}H_{13}}<\!\begin{matrix}\mathrm{CHMe}\\ \mathrm{O}\text{———}\end{matrix}\!>\mathrm{CO}$, is obtained together with methylisodesmotroposantonin, by the action of sodium methoxide and methylic iodide on desmotroposantonin,



$$\mathrm{OH{\cdot}C_{12}H_{13}}<\!\begin{matrix}\mathrm{CHMe}\\ \mathrm{O}\text{———}\end{matrix}\!>\mathrm{CO};$$

it crystallises in long needles melting at 152—153°, has the specific rotation $[\alpha]_D = +91{\cdot}9$ in absolute alcohol, and dissolves sparingly in the usual solvents. It behaves like an alkylated phenol and is but slowly converted by boiling alkalis into methyldesmotroposantonic acid. The corresponding *ethyl* derivative, $C_{17}H_{22}O_3$, is similar in preparation and properties; it crystallises in long needles melting at 168° and has the specific rotation $[\alpha]_D = +114{\cdot}0$ to $114{\cdot}2$ in absolute alcohol. The *benzyl* derivative also, prepared by the action of sodium ethoxide and benzylic chloride, crystallises in needles melting at 182°, and has the specific rotation $[\alpha]_D = +102{\cdot}6$.

Isodesmotroposantonin crystallises in needles melting at 187—188°, and in absolute alcohol has the specific rotation $[\alpha]_D = +128{\cdot}8$. It yields *methylisodesmotroposantonin*,  $\mathrm{OMe{\cdot}C_{12}H_{13}}<\!\begin{matrix}\mathrm{CHMe}\\ \mathrm{O}\text{———}\end{matrix}\!>\mathrm{CO}$, on treatment with sodium methoxide and methylic iodide; this crystallises in needles melting at 111—112°, and in alcohol has $[\alpha]_D = +118{\cdot}2$. The corresponding *ethyl* compound crystallises in hemimorphic, monoclinic prisms melting at 82°; $a:b:c = 0{\cdot}2718:1:0{\cdot}2556$; $\beta = 80°\ 20'$; it is very soluble in ether, chloroform, or alcohol, and in the latter solution has the specific rotation, $[\alpha]_D = + 129\cdot6$. The corresponding *benzyl* derivative crystallises in small needles melting at 82°, and has $[\alpha]_D = + 136\cdot5$ in alcoholic solution.

Dextrosantonous acid (compare Cannizzaro and Carnelutti, Abstr., 1883, 77) melts at 179—180° and distils unchanged at 200—260° under 5 mm. pressure; it has the specific rotation, $[\alpha]_D = + 74\cdot9$ in alcoholic solution, and has the normal molecular weight in freezing acetic acid. If santonin is reduced with tin and boiling hydrochloric acid, less santonous acid is obtained, but *paradimethylethyloethydronaphthalene*, $C_{10}H_{13}Me_2Et$, is formed; when purified from an additive compound with hydrogen chloride by fractionation from sodium, it is a limpid colourless oil which boils at 247—248° under ordinary pressure, and gives the normal vapour density by V. Meyer's method.

Methylic dextrosantonite (compare Cannizzaro and Carnelutti, *loc. cit.*), melts at 86°, and has the specific rotation $[\alpha]_D = +84\cdot9$ in alcohol. The ethylic salt gives $[\alpha]_D = +71\cdot0$ in alcohol, and the crystals phosphoresce when crushed, whilst the *benzoyl* derivative, $OBz{\cdot}C_{12}H_{14}{\cdot}CHMe{\cdot}COOEt$, melts at 75° and gives $[\alpha]_D = +59\cdot9$.

*Dextromethylsantonous acid*, $OMe{\cdot}C_{12}H_{14}{\cdot}CHMe{\cdot}COOH$, is prepared by the action of sodium methoxide and methylic iodide on dextrosantonous acid or its ethylic salt; its *ethylic* salt crystallises in prisms melting at 116—117°, is soluble in alcohol, ether, light petroleum, or cold alkaline carbonates and has the specific rotation $[\alpha]_D = + 72\cdot2$, in alcoholic solution. Dextro-ethylsantonous acid melts at 120°, and its ethylic salt has the specific rotation $[\alpha]_D = + 70\cdot5$ in alcohol.

*Ethylic dextrobromosantonite*, $OH{\cdot}C_{14}H_{17}Br{\cdot}COOEt$, prepared by brominating ethylic dextrosantonite, forms beautiful hemihedral orthorhombic crystals melting at 86°, and is very soluble in ether, alcohol, or ethylic acetate; it has the specific rotation $[\alpha]_D = +68\cdot2$ in alcohol. It is precipitated unchanged from its solution in potash by carbonic anhydride, but if the solution is heated or kept, a mixture of two isomeric dextrobromosantonous acids is obtained. *α-Dextrobromosantonous acid*, $C_{15}H_{19}BrO_3$, is very soluble in ether, from which it crystallises, with $\frac{1}{2}Et_2O$, in tablets which melt for the first time at 110°, and after solidification at 115—116°; the pure acid has the specific rotation $[\alpha]_D = + 69\cdot7$ in alcohol. *β-Dextrobromosantonous acid*, is sparingly soluble in ether, crystallises in pyramids melting at 159—160°, and has the specific rotation $[\alpha]_D = + 61\cdot9$. On treatment with alcohol and hydrogen chloride, the α-acid yields the ethylic salt from which it is prepared, whilst the β-isomeride gives a viscous uncrystallisable mass.

No crystalline products were obtained on oxidising dextrosantonous acid with permanganate, ferricyanide, or chromic acid, and on boiling the acid with iodine in acetic acid solution, a green amorphous *substance* having the composition of a dimethylnaphthaquinonepropionic acid, $C_{15}H_{14}O_4$, was formed; this dissolves in water, alcohol, and alkalis giving fluorescent solutions. On boiling dextrosantonous acid with dilute acetic acid and ferric chloride, *dextrodisantonous acid*, $COOH{\cdot}CHMe{\cdot}C_{12}H_{13}(OH){\cdot}C_{12}H_{13}(OH){\cdot}CHMe{\cdot}COOH$, is formed; it crystallises in small needles melting at 250—250·5°, is soluble in alcohol, acetic acid, or alkali carbonates, and has the specific rotation, $[\alpha]_D = +89\cdot5$ in alcohol, and the normal molecular weight in freezing acetic acid. Its *diethylic* salt, prepared by means of alcohol and hydrogen chloride, crystallises in colourless prisms melting at 183°, and depresses the freezing point of benzene normally. The two *methylic* salts melt at 158° and 215°, but were not analysed.

A comparison of the rotatory powers of the lævosantonous acid, prepared by reducing isodesmotroposantonin (Abstr., 1894, i, 205) with those of its dextro-isomeride, shows that the two substances are enantiomorphous; when crystallised together they yield the inactive isosantonous acid melting at 153—155°.

*Methylic lævosantonite* crystallises in large prisms melting at 86°, and is very soluble in alcohol, ether, or light petroleum. The *ethylic* salt crystallises in large, hemimorphic, monoclinic prisms which melt at 116—117° and become phosphorescent when crushed; $a:b:c = 0\cdot5628:1:0\cdot6959$; the specific rotation in alcohol is $[\alpha]_D = -70\cdot4$. *Ethylic lævobenzoylsantonite* crystallises in long needles melting at 75°, and has the specific rotation $[\alpha]_D = -59\cdot8$ in alcohol, that of its dextro-isomeride being $+59\cdot9$. *Ethylic lævosodiosantonite* behaves just like the dextro-compound.

*Lævomethylsantonous acid*, $OMe\cdot C_{12}H_{14}\cdot CHMe\cdot COOH$, is prepared by the action of sodium methoxide and methylic iodide on lævosantonous acid, or by reducing methylisodesmotroposantonin with zinc dust and acetic acid; it crystallises in pyramids melting at 116—117°, and is very soluble in ether. *Ethylic lævo-ethylsantonite* also prepared from lævosantonous acid, crystallises in needles melting at 31—32°, and has the specific rotation $[\alpha]_D = -70\cdot3$; the *acid* crystallises in colourless needles melting at 120°, and has the specific rotation $[\alpha]_D = -73\cdot1$. *Lævobenzylsantonous acid* is obtained as a gum. On brominating ethylic lævosantonite in carbon tetrachloride solution, *ethylic lævobromosantonite* is obtained in large, hemihedral, orthorhombic crystals, which melt at 86°, and are enantiomorphous with those of the dextro-isomeride; $a:b:c = 0\cdot5317:1:1\cdot0649$; it has the specific rotation $[\alpha]_D = -68\cdot5$, and on hydrolysis yields *lævo-α-bromosantonous acid*, which crystallises with $\frac{1}{2}Et_2O$, melts at 110—111° and 115—116° like its dextro-isomeride, and has the specific rotation $[\alpha]_D = -69\cdot4$. *Lævodisantonous acid* crystalises in needles melting at 250—250·5°, and has the specific rotation $[\alpha]_D = -85\cdot8$. The behaviour and properties of these lævorotatory substances are very similar to those of their dextro-isomerides.

The isosantonous acid of Cannizzaro and Carnelutti (*loc. cit.*) is identical with the racemic santonous acid obtained by crystallising equal weights of dextro- and lævo-santonous acid together, and melts at 153°. The *methylic* salt melts at 110·5—111°. Racemic ethylic santonite crystallises in small, colourless, anorthic crystals which melt at 125°, and do not become phosphorescent like those of its active isomerides when crushed; $a:b:c = 1\cdot6891:1:0\cdot7930$; $\alpha = 92°\ 59'$, $\beta = 112°\ 3'$, $\gamma = 85°\ 25'$; cryoscopic determinations show it to be dissociated into its components in acetic acid solution. Racemic ethylic benzoylsantonite melts at 89°.

*Racemic methylsantonous acid* crystallises in small prisms melting at 135—135·5°, and the corresponding ethyl compound melts at 144—145°, not at 143°, as previously stated; *racemic ethylic bromosantonite*, $OH·C_{12}H_{13}Br·CHMe·COOEt$, melts at 104—106°, and on hydrolysis yields *racemic α-bromosantonous acid* which melts at 193—195°. *Inactive disantonous acid* crystallises in small pyramids melting at 243—244°.

Methyldesmotroposantonous acid melts at 107—108° and has the specific rotation $[\alpha]_D = -48·9$; the corresponding *ethyl* compound, $OEt·C_{12}H_{14}·CHMe·COOH$, crystallises in large, anorthic prisms melting at 127°, and has the specific rotation $[\alpha]_D = -47·2$ in alcoholic solution; $a : b : c = 1·1269 : 1 : 0·6013$; $\alpha = 69° 40'$, $\beta = 130° 47'$, $\gamma = 119° 52'$. The *ethylic* salts of both these acids are viscous liquids.

*Benzyldesmotroposantonous acid*, $C_7H_7O·C_{12}H_{14}·CHMe·COOH$, prepared by reducing benzyldesmotroposantonin with zinc dust and acetic acid, crystallises in prisms melting at 120—121°, and has the specific rotation $[\alpha]_D = -39·3$ in alcohol.

Methylic desmotroposantonite (Abstr., 1894, i, 205) has the specific rotation $[\alpha]_D = -41·8$ in alcoholic solution; the *sodium* derivative of this and the corresponding ethylic salt are white powders. *Methylic bromodesmotroposantonite*, $OH·C_{12}H_{13}Br·CHBr·COOMe$, prepared by direct bromination, is a syrupy liquid which when hydrolysed with potash yields *bromodesmotroposantonous acid;* it crystallises with ether or petroleum, in needles melting at 92°, and has the specific rotation $[\alpha]_D = -50·4$ in alcohol.

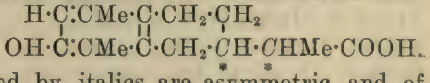
*Desmotropodisantonous acid*,

$$COOH·CHMe·C_{12}H_{13}(OH)·C_{12}H_{13}(OH)·CHMe·COOH,$$

is prepared by oxidising desmotroposantonous acid with ferric chloride; it crystallises in laminæ melting at 254—255°, and has the specific rotation $[\alpha]_D = -64·5$ in alcohol.

On heating desmotroposantonous acid at 295—305°, a resinous anhydride is obtained which, when precipitated from its sodium carbonate solution by hydrochloric acid, yields lævosantonous acid. When fused with potash, each of the four santonous acids breaks up quantitatively yielding hydrogen, propionic acid, and the same paradimethyl-β-naphthol (compare Cannizzaro and Carnelutti, *Gazzetta*, **13**, 385); it crystallises in lustrous needles melting at 135—136°, and boils at 315—316° under 760 mm. pressure; its methyl derivative crystallises in prisms melting at 68°. The same dimethylnaphthol is obtained, together with propionic acid and hydrogen bromide on fusing dextro-α-bromosantonous acid with potash; if the mixture is fused for only a short time, an ill-defined *acid*, which probably has the constitution $OH·C_{12}H_{12}·CHMe·COOH$, is obtained.

The author concludes that the four santonous acids are stereoisomerides having the constitution



$$\begin{array}{l} H·C\colon CMe·C·CH_2·CH_2 \\ OH·C\colon CMe·C·CH_2·\overset{*}{C}H·\overset{*}{C}HMe·COOH. \end{array}$$

The two carbon atoms indicated by italics are asymmetric and of different kinds; therefore four optically active and two racemic santonous acids should exist. Representing the asymmetric carbon atom of greatest optical activity by *A*, and that of lesser by *B*, dextro-

and lævosantonous acids should contain $+A\ +B$ and $-A\ -B$ respectively, whilst desmotroposantonous acid should contain $-A\ +B$; the racemic santonous acid should be compounded of $+A\ +B$ and $-A\ -B$.
W. J. P.

**Pyridine Periodides.** By Albert B. Prescott and P. F. Trowbridge (*J. Amer. Chem. Soc.*, 1895, **17**, 859—869).—*Pyridine methyl pentiodide*, $C_5NH_5,MeI,I_4$, is obtained by adding an alcoholic solution of pyridine methiodide to a solution of the requisite quantity of iodine in alcohol. After recrystallisation from alcohol, it forms long, greenish-black needles, and melts at 47·5°.

*Pyridine methyl diiodide* forms reddish-brown needles and melts at 91·5°. The crystals are very stable; after eight months, no appreciable decomposition was observable. The *triiodide* forms fine, dark red needles, is perfectly stable, and melts at 50°. *Dipyridine dimethyl enneaiodide*, $(C_5NH_5,CH_3I)_2I_7$, crystallises in greenish-black, lustrous needles, and melts at 44°. The *octaiodide* is still under investigation.

*Pyridine ethyl triiodide* melts at 49°. *Pyridine tetraiodide*, obtained by adding to pyridine an alcoholic solution of iodine until a precipitate ceased to form, crystallises in fine, dark green, lustrous needles; it is readily soluble in alcohol, ether, and chloroform, less readily in benzene, melts at 85°, and is less stable than the compounds previously described.

The authors have also prepared Dafert's pyridine hydrogen pentiodide (Abstr., 1883, 980); the analyses agree with the formula $C_5NH_5,HI,I_4$. The melting point is given as 85° (Dafert gives 89°). The paper concludes by giving instructions for the estimation of iodine in periodides.
J. J. S.

**The Pyridine Series.** By Arthur Philips (*Annalen*, 1895, **288**, 253—265; compare Abstr., 1893, i, 727, and 1894, i, 301).—The main facts recorded in this paper have been already described (*loc. cit.*).
M. O. F.

**Mercuroquinoline Compounds.** By Leone Pesci (*Gazzetta*, 1895, **25**, i, 394—406).—*Quinoline mercuric chloride*, $2C_9NH_7,HgCl_2$, is prepared by mixing alcoholic solutions of quinoline and mercuric chloride; it crystallises in colourless, thin needles or small rhombohedra, decomposes at 150—200°, and is insoluble in cold water. On mixing the proper proportions of quinoline and mercuric chloride in alcoholic solution, a *salt* of the composition $2C_9NH_7,2HgCl_2$ may be obtained; it crystallises in microscopic prisms and is soluble in boiling alcohol. On heating the first salt described above with quinoline hydrochloride in aqueous solution, a *salt* of the composition $11C_9NH_7,5HgCl_2,HCl$ is obtained; it crystallises in colourless, transparent, anorthic prisms melting at 143°, and is soluble in boiling alcohol. A *salt* of the composition $7C_9NH_7,3HgCl_2,HCl$, which crystallises in thin, colourless needles, was also prepared.

A *compound* of the composition $2C_9NH_7,HgCl_2,PtCl_4$ is deposited as a yellow, amorphous powder on mixing solutions of quinoline mercuric acetate and hydrogen platinochloride; it melts and decomposes at 140—141°.

*Quinoline mercuric nitrate*, $2C_9NH_7,Hg(NO_3)_2,2H_2O$, prepared by treating the corresponding acetate with potassium nitrate, crystallises in colourless, transparent prisms, melting and decomposing at 183—184°. *Quinoline mercuric sulphate*, $2C_9NH_7,HgSO_4$, separates in colourless octahedra on adding quinoline to mercuric sulphate solution; it melts and decomposes at 140—142°.

*Quinoline mercuric acetate*, $2C_9NH_7,Hg(OAc)_2,2H_2O$, separates in large, transparent, orthorhombic crystals on cooling a solution of quinoline in mercuric acetate solution; it is soluble in chloroform, benzene, or water, and is most soluble in water at 40°, for above this temperature the solution becomes turbid and deposits an oily substance. It melts at 148°, and is decomposed by boiling water, giving mercuric oxide, quinoline, and a *salt* of the composition

$$2C_9NH_7,2Hg(OAc)_2;$$

the latter crystallises in colourless needles melting at 156°, and may be also prepared by mixing quinoline and mercuric acetate solution in the proper proportion. *Quinoline mercuric oxalate*, $2C_9NH_7,HgC_2O_4$, prepared by the interaction of the corresponding acetate and potassium oxalate, crystallises in colourless laminæ, melting and decomposing at 177—178°.

The above compounds may be regarded as salts of *quinoline mercuric hydroxide*, $2C_9NH_7,Hg(OH)_2$, a solution of which can be readily prepared by treating the corresponding sulphate with barium carbonate; the solution is colourless, and has a strongly alkaline reaction towards litmus, but is indifferent towards phenolphthaleïn. The pure base could not be isolated, for, on evaporating the solution, quinoline and mercuric oxide separate; the base in solution reacts quantitatively with sodium thiosulphate, yielding quinoline, mercuric thiosulphate, and caustic soda; with potassium iodide, giving quinoline, mercuric iodide, and caustic potash; and with ammonium bromide, giving quinoline, mercuric bromide, and ammonia. W. J. P.

**Synthesis of Quinoline Derivatives from Anthranilic acid and Aldehydes.** By STEFAN NIEMENTOWSKI and B. ORZECHOWSKI (*Ber.*, 1895, **28**, 2809—2822; compare Abstr., 1894, i, 427).—Acetaldehyde reacts readily with anthranilic acid to form *ethylideneanthranilic acid*, $COOH{\cdot}C_6H_4{\cdot}N{:}CHMe$, which, however, could not be obtained quite pure, as it partially decomposes when recrystallised. *Trichlorethylideneanthranilic acid* is obtained from chloral and anthranilic acid; it crystallises in rhombic tablets, melts at 152°, and is decomposed by boiling water into anthranilic acid and chloroform. *Propylideneanthranilic acid* is a yellow powder which melts at 115°. When this compound or its constituents are heated on the water bath, 3′-*methyl*-2′-*ethylquinoline*-1-*carboxylic acid* is formed; it crystallises in pale yellow needles or plates, melting at 221°. This substance is accompanied by *methylethylacroleïnanthranilic acid*,

$$COOH{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}CMe{:}CHEt,$$

which is a yellow, amorphous mass, and is converted into the foregoing substance when its alcoholic solution is preserved. The carboxylic acid, on distillation, yields the 3′-methyl-2′-ethylquinoline described by Doebner and Miller (Abstr., 1884, 1376). This is accompanied by other products, which have not yet been examined.

Oenanthaldehyde reacts with anthranilic acid at the ordinary temperature to form a polymeric *heptylideneanthranilic acid*, $C_{28}H_{38}N_2O_4$, which melts at 183°, and is converted into the compound, $C_{14}H_{19}NO_2$, when it is heated for some time at its melting point; the latter crystallises well and melts at 93°. When it is heated with a strong acid or an alkali, it is converted into 3′-*amyl*-2′-*hexylquinoline*-1-*carboxylic acid*, which crystallises in rhombic tablets melting at 69°. The *hydrochloride* is formed when hydrogen chloride is passed into an ethereal solution of heptylideneanthranilic acid. The carboxylic acid may also be obtained by heating heptylideneanthranilic acid with acetic anhydride. Oxygen is absorbed from the air and acetanthranilic acid formed. On distillation, the acid yields 3′-amyl-2′-hexylquinoline. 4′-*Hydroxy*-3′-*amylquinoline* is formed in small amount when heptylideneanthranilic acid is heated at 200° in a sealed tube, and forms broad, silky needles, melting at 85°.

The author has also obtained a substance of the formula $C_{21}H_{20}N_2O_3$ by the condensation of oenanthaldehyde and anthranilic acid under conditions which have not been precisely defined. It crystallises in yellow needles melting at 243°. A. H.

**Compounds of Antipyrine (Dimethylphenylpyrazolone) with Dihydric Phenols.** By Gustave Patein and E. Dufau (*Compt. rend.*, 1895, **121**, 532—534).—*Catecholdiantipyrine* is obtained by mixing aqueous solutions of its constituents; it forms colourless crystals, which melt at 78—79°, and are very soluble in alcohol and chloroform, slightly soluble in ether or water. With ferric chloride solution, a greenish-black coloration is produced. Guaiacol or methylcatechol combines with only one molecular proportion of antipyrine, and veratrol or dimethylcatechol does not combine with it at all. Resorcinol combines with only one molecular proportion of antipyrine, and the product, which melts at 103—104°, gives a blood-red coloration with ferric chloride.

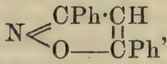
Quinol, like catechol, combines with two molecular proportions of antipyrine, and the product crystallises in colourless needles, which melt at 127—128° and are very soluble in boiling water or alcohol, slightly soluble in ether, and soluble in, but decomposed by, chloroform. With ferric chloride, a deep red coloration is produced, changing, after a time, to pale red. In presence of the slightest excess of quinol, decolorisation is instantaneous, and quinhydrone is precipitated.

These products cannot be regarded as mere molecular combinations, and it is probable that combination takes place between the hydroxyl groups and the nitrogen which is in connection with the methyl group in the antipyrine, this nitrogen becoming quinquivalent.

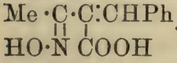
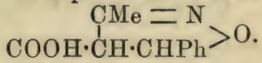
It is noteworthy that the ortho- and para-dihydric phenols combine with 2 mols. of antipyrine, whereas the metadihydric phenol combines only with one, and this power of combination disappears in proportion as the hydroxyl groups are displaced by a metal or an alkyl radicle. C. H. B.

**Diphenylisoxazole.** By CARL GOLDSCHMIDT (*Ber.*, 1895, **28**, 2540).—Benzylideneacetophenone dissolved in ether is converted by chlorine into *benzylideneacetophenone αβ-dichloride*,

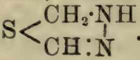
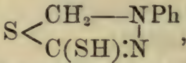
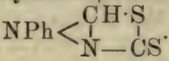
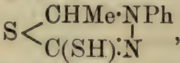
$$\mathrm{CHPhCl{\cdot}CHCl{\cdot}COPh},$$

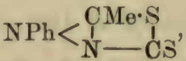
which melts at 113°. This substance reacts with hydroxylamine to form *diphenylisoxazole*,  $\mathrm{N}\!\left\langle\begin{array}{l}\mathrm{CPh{\cdot}CH}\\ \mathrm{O{-\!-}CPh}\end{array}\right.$, which crystallises in nacreous plates, melting at 141°.

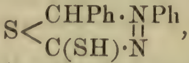
This compound and phenylmethylisoxazole are converted by alcoholic ammonia at 250° into crystalline bases, an account of which will shortly be published. A. H.

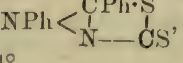
**Action of Hydroxylamine on Ethylic Benzylideneacetoacetate.** By EMIL KNOEVENAGEL and W. RENNER (*Ber.*, 1895, **28**, 2994—3000; compare R. Schiff, this vol, i, 83).—Hydroxylamine hydrochloride in alcoholic solution reacts with ethylic benzylideneacetoacetate when warmed for some 30 minutes on the water bath, the chief product being γ-methyl-β-benzylideneisoxazolone (m. p. 142°). When treated with hydroxylamine hydrochloride in the cold, ethylic benzylideneacetoacetate yields the hydrochloride of the above methyl benzylideneisoxazolone; this readily loses hydrogen chloride when suspended in alcohol, and, when warmed with a 10 per cent. sodium hydroxide solution, yields a substance which is probably the hitherto unknown labile form of *oximidobenzylideneacetoacetic acid*,  $\begin{array}{l}\mathrm{Me{\cdot}C{\cdot}C{:}CHPh}\\ \mathrm{HO{\cdot}N\ \ COOH}\end{array}$. It melts at 186°, readily dissolves in alkalis, but is insoluble in water, benzene, and light petroleum. Methyl benzylideneisoxazolone itself does not yield this acid when warmed with alkalis, but is completely decomposed. The *ammonium* salt forms colourless crystals, melts at 194—196°, and is readily soluble in water. The acid may be reconverted into methylbenzylideneisoxazolone either by treatment with an alcoholic solution of hydrogen chloride in the cold, or with aqueous hydrogen chloride at 100°. It is possible that the acid in question may have the constitution  $\left.\begin{array}{r}\mathrm{CMe = N}\\ \mathrm{COOH{\cdot}CH{\cdot}CHPh}\end{array}\right\rangle\mathrm{O}$. When an alcoholic solution of ethylic benzylideneacetoacetate is treated with free hydroxylamine at the ordinary temperature, a different product is obtained. This melts at 104—106°, and is readily soluble in alcohol, benzene, and light petroleum, but insoluble in water and ether; its constitution has not yet been determined. J. J. S.

**A Synthesis of 3 : 5-Methylphenylpyrazole.** By CARL GOLDSCHMIDT (*Ber.*, 1895, **28**, 2952).—When phenylmethylisoxazole is heated with alcoholic ammonia at 240°, oxygen is replaced by the imido-group, and 3 : 5-methylphenylpyrazole (Sjollema, Abstr., 1894, i, 546) is obtained. C. F. B.

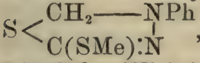
**Synthesis of Biazoline Derivatives.** By Max Busch (*Ber.*, 1895, **28**, 2635—2647).—Phenylthiocarbazinic acid, in the form of the potassium salt or an ethereal salt, reacts with aldehydes to produce derivatives of thiobiazoline,  $S<\begin{array}{l}CH_2\cdot NH\\ CH:N\end{array}$. *Phenylthiobiazoline hydrosulphide*,  $S<\begin{array}{l}CH_2—NPh\\ C(SH):N\end{array}$, formed by the action of formaldehyde on the potassium salt of phenylthiocarbazinic acid, crystallises in druses of compact, white plates melting at 112°. It readily dissolves in aqueous alkalis, and is decomposed by boiling with them into formaldehyde and phenylthiocarbazinic acid. *Phenylthiobiazoline bisulphide*, $(C_8H_7SN_2)_2S_2$, is formed by the action of ferric chloride on the hydrosulphide, and crystallises in lustrous, orange plates, melting at 135°. The bisulphide undergoes a characteristic decomposition when it is heated to 130°, or when its chloroform solution is preserved, the hydrosulphide being formed, together with *phenylisodithiobiazolone*,  $NPh<\begin{array}{l}CH\cdot S\\ N—CS\end{array}$. This substance crystallises in narrow, greenish plates, and melts and decomposes at 190°. It is insoluble in cold alkalis, but dissolves on warming, yielding a solution from which phenylthiocarbazinic acid is deposited on the addition of an acid. *Methylphenylthiobiazoline hydrosulphide*,  $S<\begin{array}{l}CHMe\cdot NPh\\ C(SH):N\end{array}$, is prepared from acetaldehyde, and forms large, feathery plates, melting at 132°. The *potassium salt* forms lustrous, white plates, and is readily soluble in water and alcohol. The *bisulphide* crystallises in orange-coloured plates, melting at 140°.

*Methylphenylisodithiobiazolone*,  $NPh<\begin{array}{l}CMe\cdot S\\ N—CS\end{array}$, crystallises in fascicular groups of light yellow plates, which melt at 216°. It does not appear to be converted into methylphenylthiobiazoline hydrosulphide by reduction. It unites with methylic iodide to form a substance of the formula, $C_9H_8N_2S_2,MeI$, which crystallises in long, lustrous needles, melting at about 180°.

*Diphenylthiobiazoline hydrosulphide*,  $S<\begin{array}{l}CHPh\cdot NPh\\ C(SH)\cdot N\end{array}$, is prepared from benzaldehyde, and crystallises in almost colourless, rhombohedral crystals, which melt at 156·5°. The *sodium salt*, $C_{14}H_{11}N_2S_2Na + 3H_2O$, forms silvery plates, and the *potassium salt* white needles. *Diphenylthiobiazoline methosulphide*, $C_{14}H_{11}SN_2\cdot SMe$, is obtained by the action of methylic iodide on the hydrosulphide, or by the condensation of benzaldehyde with methylic phenylthiocarbazinate. It crystallises in faintly yellowish-green needles, melting at 93—94°. The *bisulphide* is a lustrous brown crystalline powder, melting at 138°.

*Diphenylisodithiobiazolone*,  $NPh<\begin{array}{l}CPh\cdot S\\ N—CS\end{array}$, forms orange-coloured crystals, melting at 223—224°.

*Methylic phenylthiocarbazinate*, NHPh·NH·CSSMe, forms fascicular groups of flat needles, melting at 135°. It dissolves without change in dilute alkalis, and is much more stable than the acid. With formaldehyde, it produces *phenylthiobiazoline methosulphide*,



$S<\begin{matrix}CH_2\text{——}NPh\\ C(SMe){:}N\end{matrix}$, which crystallises in long needles, melting at 34—35°. With benzaldehyde, the methylic salt forms the diphenylthiobiazoline methosulphide described above. A. H.

**Constitution of Heteroxanthine.** By MARTIN KRÜGER and GEORG SALOMON (*Zeit. physiol. Chem.*, 1895, **21**, 169—185)—See this vol., ii, 200.

**Water of Crystallisation of Morphine Hydrochloride and of Morphine.** By WILHELM GÖHLICH (*Arch. Pharm.*, 1895, **233**, 631—645).—Results of the estimation of water of crystallisation in carefully purified morphine show that at 100° it lost from 0·017 to 2·53 per cent. in weight, and at 120° decomposed slightly, the final loss amounting to 5·89—6·34 per cent. This result is not in agreement with those of Dott (Abstr., 1888, 506) and Dieterich (*Helf. Ann.*, 1888), who record instances of a loss of the total water at 100°, and a loss in weight at 120° of 6·39—6·56 per cent. Estimations made with morphine hydrochloride showed a loss in weight varying from 13·02 to 14·23 per cent. The number calculated from the usually accepted formula, $C_{17}H_{19}NO_3,HCl + 3H_2O$, being 14·38. The author concludes that specimens of morphine hydrochloride, as described by the German Pharmacopœa, containing from 14·5—15 per cent. of water, are of the rarest occurrence. A. L.

**Papaveraldoxime.** By ROBERT HIRSCH (*Monatsh.*, 1895, **16**, 828—848).—The oxime obtained from Goldschmiedt's papaveraldine (compare Abstr., 1887, 163) consists of two stereoisomerides, of which one crystallises in very slender, microscopic needles, and melts at 235°; the other crystallises in large, flat prisms, and melts at 254°. From either of these stereoisomerides, by interaction with hydrochloric acid under suitable conditions, the following four hydrochlorides can be prepared :—A *monohydrochloride*, $C_{20}H_{20}N_2O_5,HCl + 3H_2O$, which forms small, needle-shaped, yellow crystals; a *monohydrochloride*, $C_{20}H_{20}N_2O_5,HCl + 10H_2O$, which crystallises in colourless, rhombic prisms, sinters at 90°, and melts and decomposes at 220—225°; a *dihydrochloride*, $C_{20}H_{20}N_2O_5,2HCl + 12H_2O$, which crystallises in yellow, silky, flat needles, melts in its water of crystallisation at 80—86°, evolves gas at 109°, again solidifies at a higher temperature, and finally melts and decomposes at 210—230°; and a *dihydrochloride*, $C_{20}H_{20}N_2O_5,2HCl + 4H_2O$, which crystallises in yellow, rhombic plates, melts at 95°, evolves gas at 110°, and completely decomposes at 210°. All these hydrochlorides when heated at 110°, lose water, or water and hydrogen chloride, and form the same anhydrous monohydrochloride. Attempts to ascertain the configuration of the stereoisomeric papaveraldoximes led to no certain results.

When reduced with sodium amalgam in acid solution, papaveraldoxime is converted into *papaveraldylamine*,

$$C_9NH_3(OMe)_2{\cdot}CH(NH_2){\cdot}C_6H_3(OMe)_2$$

$[(OMe)_2 : N : CH = 2 : 3 : 2' : 1'$ and $CH : (OMe)_2 = 1 : 3 : 4]$, a yellowish-brown oil, of vanilla-like odour, which solidifies in an exsiccator to a yellowish-brown mass melting at 80—85°.

G. T. M.

**History of Aconitine.** By MARTIN FREUND (*Ber.*, 1895, **28**, 2537—2539; compare Abstr., 1895, i, 254).—The author tabulates the results of his analyses of aconitine and some of its derivatives, and compares them with the numbers calculated from the formula proposed by himself, and from that proposed by Wright and adopted by Dunstan. He considers that the results establish the correctness of his formula.

A. H.

**Chemistry of Ipecacuanha.** By BENJAMIN H. PAUL and ALFRED J. COWNLEY (*Pharm. J. Trans.*, 1894, [3], **25**, 111—115, 373—374, 690—692).—The authors' earlier conclusion (Abstr., 1894, i, 155) as to the existence of at least two alkaloïds in the substance known as emetine, is confirmed. The separation and properties of these alkaloïds are now described. One is a base insoluble in caustic alkalis, and uncrystallisable, for which it is proposed to retain the name of *emetine;* its formula is $C_{15}H_{22}NO_2$; the other, *cephaeline*, $C_{14}H_{20}NO_2$, is soluble in caustic alkali, and obtainable in a crystalline form. These were separated from ipecacuanha by extraction with alcohol, precipitation with basic lead acetate, evaporation of the filtrate to dryness, and treatment of the residue with dilute acid; the solution was mixed with ether, ammonia added in slight excess, and shaken, and from the separated ethereal solution, dilute sulphuric acid took up the emetine, which was precipitated by soda in excess, and subjected to further treatment, in order to entirely remove the other base. The alkaline solution, when acidified and then shaken with ether and ammonia, gave cephaeline. Emetine melts at 68°, is amorphous, strongly alkaline, and colourless, but turns yellow when exposed to light. It is soluble in alcohol, ether, chloroform, or benzene, but only sparingly so in hot light petroleum or in water. Of its salts only the chloride and nitrate could be obtained in a crystalline state. Cephaeline is colourless, but, like emetine, is turned yellow by exposure to light; it is less soluble in ether, and cold light petroleum dissolves it very sparingly, whilst the hot liquid dissolves more of it, but on cooling, deposits it again in a flocculent form. It melts in a capillary tube at 96—98°, loses weight at 100° when heated in the open, and at 120° is changed, without melting, into a brown substance. The salts of cephaeline much resemble those of the other base, but its platinochloride is of a much darker yellow colour than the corresponding emetine salt.

In the second paper is noted the facility with which the chlorides of each base can be obtained as crystals from solutions containing excess of hydrochloric acid. The authors also criticise certain results published by Kunz-Krause (Abstr., 1895, i, 118) as quite incompatible with their own observations.

The remaining paper announces the isolation of a third alkaloïd from ipecacuanha. It exists in relatively small quantity, is characterised by very sparing solubility in ether, and remains in the ammoniacal liquor from which emetin and cephaeline have been extracted by ether. It can be obtained in pale yellow, prismatic crystals which melt at about 138°. Emetine, cephaeline, and their salts are already supplied commercially as medicines. R. R.

**Deliquescent Alkaloïd from Lupinus albus.** By ARTURO SOLDAINI (*Gazzetta*, **25**, 1895, i, 352—364).—The high melting hydrobromide of the deliquescent alkaloïd obtained from the seeds of *Lupinus albus* melts and decomposes at 233—234°, not at 224—225°, as previously stated (Abstr., 1893, i, 739); it has the specific rotation $[\alpha]_D = -5\cdot6°$ in a 25 per cent. aqueous solution. The *platinochloride*, $(C_8H_{13}NO)_2,H_2PtCl_6 + 2\frac{1}{2}H_2O$, is obtained as a red, crystalline powder, and when anhydrous decomposes at 202—203°; the *aurochloride* decomposes at about 163°, and is reduced by boiling with water. The *hydrochloride* crystallises in thin, prismatic needles which decompose at 165°, is insoluble in cold alcohol, and is lævorotatory in solution. The base seems therefore to be distinct from its isomeride, tropine.

The alcoholic mother liquors obtained during the preparation of the above hydrobromide contain two bases which can be separated by fractional crystallisation of their platinochlorides. One of these yields a *hydrochloride*, soluble in alcohol, which gives a crystalline *platinochloride* $(C_7H_9NO)_2,H_2PtCl_6$; the other yields a crystalline *hydrochloride*, $C_8H_{15}NO,HCl$, melting at 178°, and is insoluble in alcohol. W. J. P.

**Extraction of Alkaloïds from the Seeds of Lupinus albus.** By ARTURO SOLDAINI (*Gazzetta*, 1895, **25**, i, 365—380).—The best method of separating the alkaloïds from *Lupinus albus* is to treat the aqueous extract of the lupine meal with lime, extract with petroleum, and then to extract the latter solution with dilute hydrochloric acid; the acid solution yields the crude mixture of hydrochlorides on evaporation. The deliquescent alkaloïd is less soluble in petroleum than the crystalline one, and the bases may be separated by crystallisation from this solvent. Other methods of extracting the alkaloïds are referred to, depending on the use of basic lead acetate, Meyer's reagent, alcoholic hydrochloric acid, and dialysis. W. J. P.

**Formation of Arginine from Proteïd Substances.** By SVEN G. HEDIN (*Zeit. physiol. Chem.*, 1895, **21**, 155—168; compare Abstr., 1895, i, 160).—The substance previously obtained by the author from horny substance is proved to be identical with Schulze and Steiger's arginine (Abstr., 1886, 725). Besides the compounds mentioned by Schulze and Steiger, the author describes the compounds $AgNO_3,C_6H_{14}N_4O_2 + \frac{1}{2}H_2O$, $AgNO_3,C_6H_{14}N_4O_2,HNO_3$, and $C_6H_{14}N_4O_2,2HNO_3$. The sulphate and oxalate could not be obtained in a crystalline form. Methods for the preparation of arginine from various sources are given.

| | | | |
|---|---|---|---|
| Horn yields at least ............ | 2·25 | per cent. of | arginine. |
| Glue „ ............ | 2·60 | „ | „ |
| Conglutin yields at least ........ | 2·75 | „ | „ |
| Albumin (from yolk of egg) yields at least...................... | 2·3 | „ | „ |
| Albumin (from white of egg) yields at least...................... | 0·8 | „ | „ |
| Dry blood serum ................ | 0·7 | „ | „ |
| Caseïn ........................ | 0·25 | „ | „ |

The arginine is best isolated in the form of the silver salt, $AgNO_3,C_6H_{14}N_4O_2 + \frac{1}{2}H_2O$, as this is very sparingly soluble in water, care must be taken that the silver salt $AgNO_3,C_6H_4N_4O_2,HNO_3$ is not formed, as this is readily soluble. To accomplish this, the phosphotungstic acid precipitate is treated with barium hydroxide, the excess of hydroxide is removed by slightly acidifying with sulphuric acid, and then the sulphuric acid is exactly precipitated with barium hydroxide, and the strongly alkaline filtrate treated with silver nitrate, when the sparingly soluble silver salt is thrown down.

J. J. S.

**Anhalonium Lewinii and other Cacti.** By LOUIS LEWIN (*Chem. Centr.*, 1895, i, 219—220; from *Arch. Exp. Pathol.*, **34**, 374—391).—Crystals of anhalonine are biaxial and optically active, and belong to the rhombic system. Anhalonine dissolves in water, and gives an alkaline reaction; it is also readily soluble in alcohol, ether, chloroform, &c. The free base may be distilled without undergoing decomposition; it sinters at 74°, and is completely fused at 77·5°. The *hydrochloride*, $C_{12}H_{15}NO_3,HCl$, which tastes slightly bitter, melts and decomposes at 254—255°; it is sparingly soluble in cold water, readily in hot, crystallises from water more readily than the alkaloïd, the solution being lævorotatory, and is coloured yellow by sulphuric acid; $[\alpha]_D = -40\,56^\circ$ in alcoholic solution. Nitric acid gives first a pale red, which changes to a blood red, and, on warming, to a yellow coloration. The *platinochloride*, $(C_{12}H_{15}NO_3)_2,H_2PtCl_6$, is crystalline. In small doses, anhalonine produces reflex irritability, and in larger doses, reflex tetanus; the fatal dose for rabbits is 0·16—0·2 gram per kilo. of body weight. The same base may also be obtained from *Anhalonium Jourdanianum*.

J. J. S.

**Lithofellic acid.** By E. JÜNGER and A. KLAGES (*Ber.*, 1895, **28**, 3045—3049).—Lithofellic acid, $C_{20}H_{36}O_4$, has been studied by Goebel, Wöhler, Roster, Grattola, and Strecker; it is obtained from gallstones, and when crystallised from alcohol melts at 199° (uncorr.). When an alcoholic solution of lithofellic acid is heated with aqueous barium hydroxide for several hours in a reflux apparatus, ethylic alcohol is eliminated, and an unsaturated *acid*, $C_{18}H_{30}O_3$, is produced; it crystallises in nacreous scales, and melts at 152°.

*Lithofellolactone*, $C_{20}H_{34}O_3$, is obtained by heating an alcoholic solution of lithofellic acid with concentrated hydrochloric acid on the water bath; it is a colourless viscous oil, which boils at 245—248° under a pressure of 16 mm. The molecular refraction M = 91·99. Aqueous barium hydroxide converts the lactone into the unsaturated acid, and this substance also yields a *lactone* which boils at 275—280° under a pressure of 60 mm. M. O. F.

**Emulsin from Fungi.** By EMILE E. BOURQUELOT and H. HÉRISSEY (*Compt. rend.*, 1895, **121**, 693—695).—*Aspergillus niger* was cultivated in Raulin's fluid, and when it had fructified, the liquid was drawn off, the residue washed several times with distilled water, and finally allowed to remain in contact with distilled water for several days, the solution of emulsin thus obtained being used for the experiments. This solution hydrolyses amygdalin, salicin, coniferin, arbutin, esculin, helicin, populin, and phloridzin, but has no action on solanin, hesperidin, convallamarin, convolvulin, jalapin, and potassium atractylate. Unlike the emulsin of almonds, it has no hydrolysing action on milk sugar, and it also differs in acting, although very slowly, on populin and phloridzin.

The juice expressed from *Polyporus sulphureus*, &c., which grows on most of the ordinary trees, has similar hydrolysing properties, and acts readily on amygdalin, esculin, arbutin, coniferin, and salicin, but has no effect on milk sugar.

It follows from these and previous observations (Abstr., 1894, ii, 63, 109), that fungi all contain the same emulsin, but the evidence is not yet sufficient to decide whether it is or is not identical with the emulsin from bitter almonds. C. H. B.

**Enzymes of Certain Yeasts.** By EMIL FISCHER and PAUL LINDNER (*Ber.*, 1895, **28**, 3034—3039).—The authors give details of 24 experiments intended to throw light on the question whether the fermentation of polysaccharides is preceded by hydrolysis. They find that melibiose is hydrolysed by extracts of the yeasts (Frohberg and Saaz) of bottom fermentation; the extracts were prepared by digesting with water at 33° for 20 hours specimens which were dried for three days in air at 20—25°, having been previously drained on porous earthenware. As these types also induce hydrolysis when employed in the moist state, it is evident that the hydrolytic enzyme is not a result of desiccation. Melibiose, however, is indifferent towards the Frohberg and Saaz types of top fermentation yeast, neither the fresh product nor an aqueous extract of the dried yeast effecting hydrolysis of the sugar; this observation contradicts the statement of Scheibler and Mittelmeier (Abstr., 1890, 226), who recorded the complete hydrolysis of melibiose by the agency of invertin, an enzyme which is present in the types indicated. Moreover, the authors have repeated the experiment of Scheibler and Mittelmeier with a negative result, and are led, therefore, to the conclusion that the specimen of invertin which these investigators employed was contaminated with other enzymes of beer yeast.

An aqueous extract of desiccated *Monilia candida* has no action on cane sugar, but the dried product contains a hydrolytic enzyme which is, therefore, insoluble in water; a fresh specimen of the moist yeast also hydrolyses cane sugar, although less actively than the dried substance. All three preparations of this yeast, however, have a marked hydrolytic action on maltose. *Saccharomyces apiculatus*, whether dry or fresh, is without hydrolytic action on cane sugar.

In the course of these experiments, thymol and toluene have been employed as anæsthetic agents to prohibit fermentation.

M. O. F.

**Liquefaction and Saline Digestion of Gelatin.** By A. Dastre and N. Floresco (*Compt. rend.*, 1895, **121**, 615—617).—The liquefaction of gelatin, or loss of the power of gelatinisation, is brought about by the prolonged or repeated action of boiling water, the brief action of water at a high temperature, the action of certain saline solutions, and also, as is well known, by the action of liquefying bacteria, and by gastric or pancreatic digestion.

Gelatinisation begins to be apparent with solutions containing 0·75 part of gelatin in 100; solutions containing 5 to 10 parts per 100 are strong solutions in which the phenomena can be easily followed, whilst solutions containing 2·3 parts per 100 may be regarded as of medium concentration.

The liquefaction is due to the conversion of the gelatin, by combination with water, into gelatose or protogelatose, which is characterised by the fact that it will not gelatinise and is not precipitated by a saturated solution of sodium chloride, complete liquefaction corresponding with complete conversion into gelatose. The same change is produced by liquefying bacteria.

Contrary to the usual belief, comparatively short exposures of gelatin to such temperatures as 110—120° causes a partial conversion of gelatin into gelatose with consequent loss of gelatinising power, and there is little doubt that any contact with warm water does affect the gelatin, although the effect may not be at once appreciable.

In contact with certain salts, such as alkali chlorides or iodides, gelatin gradually loses its power of solidifying. With solutions containing only 1 part of salt per 100, the effect on the gelatin is shown by the greater time required for gelatinisation and the lower consistency of the jelly. With 10 parts of salt per 100 liquefaction is complete, and the gelatin is entirely converted into gelatose whatever the proportion of gelatin used. It is noteworthy, however, that with alkali fluorides, the change is never complete. To this phenomenon the authors give the name *saline digestion*, because it is identical in its results with gastric and pancreatic digestion, and is produced under similar conditions, that is to say, by prolonged contact at a moderate temperature, such as 40°, but not by short exposure to a high temperature such as 100—120°.

C. H. B.

# Organic Chemistry.

**Sodium Nitroferrocyanide.** By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1896, **11**, 31—36; see also this vol., i, 69).—A *compound*, $Fe(CN)_5Na_5SO_3 + 9H_2O$, is obtained by adding sodium nitroferrocyanide (20 grams) to a 40 per cent. solution of sodium hydrogen sulphite (50 grams), neutralising with sodium hydroxide, and adding 20 c.c. more of a 10 per cent. solution of sodium hydroxide. The intensely yellowish-red solution is evaporated in a vacuum over sulphuric acid, and the red crystals of the compound, after separating them from the sodium sulphate, recrystallised, taking care that the solution is not heated above 30°. It crystallises in long, thin, pale yellow needles, does not yield ammonia when heated with sodium hydroxide, gives a yellowish-green solution with hydrochloric acid, and then evolves sulphurous anhydride, a beautiful red coloration when boiled with hydroxylamine and sodium hydroxide, a bluish-white precipitate with ferrous sulphate, and a dark blue precipitate with ferric chloride. It remains entirely unaltered when treated with sodium hydrogen sulphite. When treated with iodine, the ferro-compound is converted into a ferri-compound, and with permanganate in acid solution, it yields a ferri-compound and sulphate. When treated with hydrogen peroxide, it remains for the most part unaltered. When treated with nitrous acid or nitric oxide, it yields sodium nitroferrocyanide. E. C. R.

**Preparation of Platinocyanides.** By ARNULF SCHERTEL (*Ber.*, 1896, **29**, 204—205).—These salts can be prepared very easily by dissolving well washed and freshly precipitated platinum sulphide in a solution of the corresponding cyanide, and concentrating the colourless solution; $PtS_2 + 5KCN = K_2Pt(CN)_4 + K_2S + KCNS$. $K_2Pt(CN)_4,3H_2O$, and $BaPt(CN)_4$, were so prepared. If commercial potassium cyanide, which at the present time (in England also ?) is nearly half sodium cyanide, is used, crystals of the salt $KNaPt(CN)_4,3H_2O$ are obtained, and, from the mother liquor of these, crystals of $Na_2Pt(CN)_4$. C. F. B.

**Organic Compounds containing Quadrivalent Oxygen.** By F. ZECCHINI (*Gazzetta*, 1895, **25**, ii, 58—63).—Friedel (Abstr., 1875, 1245) obtained a liquid boiling at −1° to −3° by the action of dry hydrogen chloride on dry methylic alcohol at −20° which was so unstable at ordinary temperatures that it could not be ascertained whether it consisted of the compound MeOH,HCl, containing quadrivalent oxygen. The author has repeated Friedel's experiment, and has also investigated the action of methylic iodide on methylic ether at −18°; in the latter case, a liquid is obtained by distillation, which boils at 0° to 1°, and contains iodine, but does not lend itself to further examination.

Determinations of the depression of the freezing points of various solvents by mixtures of methylic ether with hydrogen chloride or methylic iodide seem to indicate that at the temperature of the freezing solvent no combination exists. W. J. P.

**Rhodinol or Geraniol.** By Hugo Erdmann and P. Huth (*J. pr. Chem.*, 1896, [2], **53**, 42—46; compare Tiemann and Semmler, Abstr., 1895, i, 646).—Rhodinol and geraniol will combine with dibasic acids to form acid ethereal salts; such a compound with camphoric acid has been analysed.

*Rhodinol diphenylurethane*, $NPh_2\cdot CO\cdot OC_{10}H_{17}$, crystallises in long, silky, felted needles, and melts at 83—84°. This compound has been obtained from rhodinol, geraniol, and reuniol, as well as from German and Turkish rose oil. It is thus proved that "reuniol" is identical with rhodinol, so that this name must be erased from scientific literature (compare Hesse, Abstr., 1895, i, 186).

A. G. B.

**Composition of Wool Fat.** By L. Darmstaedter and Isaac Lifschütz (*Ber.*, 1895, **28**, 3133—3135).—On hydrolysing wool fat, the authors obtained an *alcohol*, $C_{10}H_{20}O$, which melts at 105—109°, and appears to be unsaturated; an *alcohol*, $C_{11}H_{22}O$, which crystallises in needles, and melts at 82—87°, has been also isolated. The authors regard these alcohols as lower homologues of lanolinic alcohol (Marchetti, Abstr., 1895, i, 408). M. O. F.

**Reduction of Pseudonitroles to Ketoximes.** By Roland Scholl and Karl Landsteiner (*Ber.*, 1896, **29**, 87—90).—In order to throw light on the structure of the pseudonitroles, the authors have submitted propylpseudonitrole to reduction; employing free hydroxylamine and potassium hydrosulphide, they obtained acetoxime in each case. M. O. F.

**Pseudonitroles and Dialkyldinitromethanes.** By Georg Born (*Ber.*, 1896, **29**, 90—102; compare the foregoing abstract, and Abstr., 1895, i, 445).—The resemblance between nitrosobenzene and the pseudonitroles, and the reduction of the latter to ketoximes with hydroxylamine or potassium hydrosulphide, lead the author to advocate V. Meyer's expression for the structure of pseudonitroles, which represents them as nitro-nitroso-compounds; moreover, oxidation of the pseudonitroles gives rise to dialkyldinitromethanes, and these also, when reduced, yield ketoximes.

*Diethyldinitromethane*, $CEt_2(NO_2)_2$, is obtained by oxidising amyl-β-pseudonitrole with chromic acid in glacial acetic acid; it is a colourless liquid, which boils at 207—208° under a pressure of 723 mm., and has an agreeable, camphor-like odour.

*Ethylpropylpseudonitrole* (*amyl-α-pseudonitrole*),

$$NO\cdot CMe(NO_2)\cdot CH_2Et,$$

is prepared by submitting an ethereal solution of methylpropylketoxime to the action of a current of nitric peroxide; it is a deep blue oil, which becomes green and decomposes in sunlight, and yields brown gas when heated at 59°. Oxidation, with chromic acid, in glacial acetic acid solution, gives rise to *methylpropyldinitromethane*, a colourless oil, which boils at 207·5—209·5° under a pressure of 723 mm., and has a pleasant odour resembling that of camphor.

as-*Dimethylpropylpseudonitrole* (*isoamylpseudonitrile*),

$NO{\cdot}CMe(NO_2){\cdot}CHMe_2$,

is a blue oil, which decomposes at 60°; on oxidation it yields *methylisopropyldinitromethane*, a pale green liquid, which solidifies in a mixture of ice and salt, and boils at 205—207° under a pressure of 724 mm.

*Diethylpropylpseudonitrole* (*heptylpseudonitrole*),

$CH_2Et{\cdot}C(NO)(NO_2){\cdot}CH_2Et$,

separates from ether in white rhombohedra, which melt, forming a blue liquid, and evolving gas, at 72—73°; during the preparation of this substance, the nitrimine is formed (compare *loc. cit.*), together with a mixture of dipropyl ketone and *dipropyldinitromethane.* The latter substance is also obtained by the oxidation of diethylpropylpseudonitrole; it is a colourless oil, which has an agreeable, camphor-like odour, and boils at 220—221°. Oxidation of the pseudonitrole is also attended with regeneration of dipropyl ketone, and reduction with free hydroxylamine or alkali hydrosulphides gives rise to dipropylketoxime.

*Tetramethylpropylpseudonitrole*, $CHMe_2{\cdot}C(NO)(NO_2){\cdot}CHMe_2$, is a pungent, blue oil, which decomposes at 54°; oxidation converts it into *diisopropyldinitromethane*, which boils and partly decomposes at 203—207° under a pressure of 717 mm. Diisopropyl ketone is also produced by oxidation of the pseudonitrole.

*Methyl α-ethylpropyl ketoxime*, $CHEt_2{\cdot}CMe{:}NOH$, is a colourless liquid, which boils at 186—188·5° (uncorr.) under a pressure of 712 mm. The action of nitric peroxide gives rise to a green oil consisting of the impure pseudonitrole, which decomposes at 67°, and when oxidised yields *methyl-α-ethylpropyldinitromethane;* this substance is a yellow oil, which boils at 211—219° under a pressure of 722 mm.

*Amylpropylpseudonitrole* (*octyl-α-pseudonitrole*),

$NO{\cdot}CMe(NO_2){\cdot}CH_2{\cdot}C_5H_{11}$,

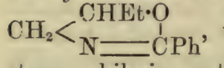
obtained from methyl hexyl ketoxime, is a blue oil, which decomposes at 53—55°, and solidifies in a freezing mixture; oxidation converts it into *methylhexyldinitromethane*, a yellowish-brown oil, which decomposes at 180°, yielding methyl hexyl ketone. M. O. F.

**β-Ethoxybutylamine and γ-Ethoxybutylamine.** By S. BOOKMAN (*Ber.*, 1895, **28**, 3111—3121; compare Abstr., 1895, i, 190).—When ethylic chloro-*sec*-butylic ether, $CH_2Cl{\cdot}CHEt{\cdot}OEt$, is heated in sealed tubes with alcoholic ammonia for three hours at 140°, β-ethoxybutylamine and di-β-ethoxybutylamine are produced.

*β-Ethoxybutylamine*, $OEt{\cdot}CHEt{\cdot}CH_2{\cdot}NH_2$, is a highly refractive liquid, which boils at 139—141°, and has a sp. gr. = 0·8505 at 16°; it readily absorbs atmospheric carbonic anhydride, and dissolves sparingly in water. The *hydrochloride* crystallises in white plates, and the *platinochloride* is extremely soluble in water; the *picrate* crystallises from hot water in lemon-yellow needles, and melts at 156°. The *phenylthiocarbamide* crystallises in lustrous, white needles, and melts at 94°.

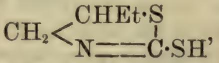
*β-Chlorobutylamine* is obtained in the form of the *hydrochloride* by heating β-ethoxybutylamine (2 grams) with fuming hydrochloric acid (20 c.c.) for 2½ hours at 150—160°; the *picrate* melts at 142°, and the *platinochloride* crystallises in yellow leaflets. When heated in sealed tubes at 100° with aqueous alkali, the hydrochloride of the base yields α-crotylamine (compare Abstr., 1892, 33).

*β-Bromobutylamine hydrobromide* is formed when β-ethoxybutylamine is heated with hydrobromic acid; the *picrate* melts at 150—151°, and decomposes at 210°. When an aqueous solution of the hydrobromide is agitated with alkali and benzoic chloride, the *benzoyl* derivative is produced, and this yields *β-μ-ethylphenyloxazoline*,



$CH_2<\begin{matrix}CHEt\cdot O\\ N=\!=\!=\!CPh\end{matrix}$, when submitted to the action of a current of steam while in contact with alkalis. The *picrate* of this base crystallises in long needles, and melts at 168°.

*β-Ethylthiazoline μ-hydrosulphide*,



$CH_2<\begin{matrix}CHEt\cdot S\\ N=\!=\!=\!C\cdot SH\end{matrix}$, is obtained by the action of carbon bisulphide on the hydrobromide of β-bromobutylamine in presence of alkali; oxidation with bromine water converts this substance into the *β-ethyltaurine*, $HSO_2\cdot CHEt\cdot CH_2\cdot NH_2$, which crystallises from water, and decomposes at 285°.

*Di-β-ethoxybutylamine*, $NH(CH_2\cdot CHEt\cdot OEt)_2$, is a feebly refractive liquid, which boils at 230°, and has a sp. gr. = 0·87 at 16°. The *hydrochloride* is white; the *aurochloride* is orange, and melts at 113°; the *picrate* is yellow, and melts at 83—85°; and the *nitrosamine* is a viscous oil which boils at 259°; when heated with fuming hydrochloric acid, the base yields a substance which is probably di-β-chlorobutylamine, the *aurochloride* of which melts at 170—171°. An unsaturated base (probably consisting of dicrotylamine) is obtained on heating di-β-ethoxybutylamine with hydrobromic acid at 140°, and distilling with potash the hydrobromide thus obtained; the *picrate* crystallises in yellow prisms, melts at 172—173°, and decomposes at 225°.

*γ-Ethoxybutylamine* is obtained by reducing the nitrile of γ-chlorobutyric acid with sodium and alcohol, butylamine being formed at the same time; it boils at 148°, and has an ammoniacal odour. The *oxalate* melts at 198—200°, the *platinochloride* at 190°, and the *thiocarbamide* at 91—92°. Fuming hydrochloric acid at 150° converts the base into ethylic chloride and γ-chlorobutylamine. M. O. F.

**Alkyl Derivatives of Ethylenediamine.** By Paul Schneider (*Ber.*, 1895, **28**, 3072—3078; compare Hinsberg, this vol., i, 47).—Diphenylsulphonethylenediamine, $C_2H_4(NH\cdot SO_2Ph)_2$, was prepared by Hinsberg's reaction (Abstr., 1892, 64) from ethylenediamine and benzenesulphonic chloride, and was converted by warming with methylic iodide and aqueous-alcoholic soda into *diphenylsulphonedimethylethylenediamine*, $C_2H_4(NMe\cdot SO_2Ph)_2$, melting at 131°. This, by heating with strong hydrochloric acid, was hydrolysed, yielding *dimethylethylenediamine*, $C_2H_4(NHMe)_2$, the *hydrochloride* of which melts and decomposes at 235—236°; the orange-red *platinochloride*, with $4H_2O$, darkens when anhydrous at 205°, and melts and decomposes at

209°; the yellow *aurochloride* crystallises with $H_2O$; the yellow *picrate* melts at 215—216°. The base itself, a diacid one, was prepared by distilling the hydrochloride with powdered potassium hydroxide and soda-lime from a copper retort; it boils at 119°, and has a sp. gr. = 0·848 at 4°, and 0·828 at the ordinary temperature (water at 4° = 1); it attracts water and carbonic anhydride from the air, and, with nitrous acid in concentrated solution, it yields yellowish-green *dimethylethylenedinitrosamine*, $C_2H_4(NMe{\cdot}NO)_2$, melting at 60—61°, showing that it is a di-secondary, and not a primary-tertiary base.

The analogous ethyl derivatives were also prepared before the publication of Hinsberg's paper. Diethylethylenediamine boils at 149—150°; the orange-red *platinochloride* melts at 223—224°, and the *aurochloride* at 220°; the *dinitrosamine* was obtained as a yellowish-green oil which decomposed on heating.

Ethylenediamine forms a *mercurochloride*, $C_2H_4(NH_2)_2,2HCl,HgCl_2$, which melts at 297°.

*Hexamethylethylenediammonium chloride*, $C_2H_4(NMe_3Cl)_2$, was prepared by the action of silver chloride on the iodide (Hofmann, *Jahresbericht*, 1859, 386); the *platinochloride* blackens at 260°, and melts and decomposes at 286°; the *picrate* melts at 262°.

C. F. B.

**Lysidine.** By Albert Ladenburg (*Ber.*, 1895, **28**, 3068—3070).—If lysidine, $C_2H_4{<}\genfrac{}{}{0pt}{}{NH}{N}{\geqslant}CMe$ (Abstr., 1895, i, 73), is shaken with benzoic chloride and potassium carbonate, it yields *acetodibenzoethylenediamine*, $NHBz{\cdot}C_2H_4{\cdot}NAcBz$, melting at 113—114°, and when this is shaken with sodium hydroxide, it is converted into dibenzoethylenediamine, $C_2H_4(NHBz)_2$, melting at 244°; this is very sparingly soluble in alcohol, and its formation can be used to detect lysidine in a 0·1 per cent. solution (which must of course contain no ethylenediamine); it is only necessary to shake the solution with benzoic chloride and sodium hydroxide.

When lysidine hydrochloride is submitted to dry distillation, it is decomposed into ammonium chloride and methylic cyanide; acetylene, or a polymeride of that substance, is presumably formed in addition, but no proof of this could be obtained. C. F. B.

**Preparation of Ethereal Salts.** By Emil Fischer and Arthur Speier (*Ber.*, 1895, **28**, 3252—3258).—The experiments detailed below show that the use of mineral acid in excess is frequently unnecessary, and sometimes decreases the yield of ethereal salt. The yield of ethylic benzoate prepared by the ordinary method with hydrogen chloride and sulphuric acid is 73 and 76 per cent. respectively, but, when benzoic acid is boiled with alcohol (2 parts) containing hydrogen chloride (3 per cent.), the yield is 76 per cent., and with sulphuric acid (10 per cent.), after heating during three hours, the yield is 90 per cent. of the theoretical. In the following table, the yield refers to the purified salt; only the authors' best results are given, but these could probably often be improved if the conditions were modified. Absolute ethylic alcohol was always employed, and the solution boiled, unless otherwise stated.

| Acids. | Alcohol. | Mineral acid. | Hours boiled. | Yield per cent. |
|---|---|---|---|---|
| α-Naphthoic, 10 grams...... | 30 grams | 0·9 gram HCl | 4 | 74·8 |
| Phenylacetic, 10 „ ...... | 30 „ | 0·9 „ „ | 4 | 87·0 |
| Cinnamic, 15 grams ........ | 45 „ | 4·5 „ $H_2SO_4$ | 5 | 89·7 |
| Crotonic, 5 grams .......... | 15 „ | 1·5 „ „ | 4 | 54·3 |
| Mandelic, 5 grams.......... | 15 „ | 0·15 „ HCl | 4 | 67·5 |
| Salicylic, 10 „ .......... | 30 „ | 6·0 „ $H_2SO_4$ | 4 | 54·0 |
| „ 10 „ .......... | 100 „ | 5·0 „ HCl | 4 | 54·5† |
| Glycollic, 10 „ .......... | 30 „ | 0·3 „ „ | 4 | 65·8 |
| Levulinic, 10 „ .......... | 30 „ | 0·3 „ „ | 4 | 76·5 |
| Succinic, 10 „ .......... | 50 „ | 0·5 „ „ | 4 | 73·9 |
| „ 10 „ .......... | 40 „ | 0·4 „ $H_2SO_4$ | 4 | 73·9 |
| Fumaric, 10 „ .......... | 40 „ | 0·4 „ HCl | 4 | 68·2 |
| Citric, hydrated, 10 grams... | 40 „ | 1·2 „ „ | 4 | 67·3 |
| Phthalic, anhydride, 10 grams | 50 „ | 1·5 „ „ | 4 | 63·3 |
| Terephthalic, 3 grams....... | 18 „ | 0·54 „ „ | 50* | 74·7 |
| Malic, 10 grams............ | 40 „ | 0·4 „ „ | 4 | 70·5 |
| Tartaric, 20 grams.......... | 80 „ | 0·8 „ „ | 4 | 72·8 |
| Mucic, 5 grams ............ | 25 „ | 0·75 „ „ | 12 | 47·3 |
| „ 5 „ ............ | 25 „ | 0·75 „ „ | 24* | 90·8† |

A considerable loss of ethylic glycollate occurs, on account of its great volatility; it has not been previously prepared from the free acid. The use of mineral acid is not advantageous in the preparation of ethylic pyruvate; the best yield is obtained by heating the acid and alcohol at 100°. The use of a sealed tube for the etherification of terephthalic acid is necessary, as, with a reflux apparatus, violent bumping occurs. Limpricht has stated that mucic acid is not etherified by the action of hydrochloric acid, or sulphuric acid, and alcohol; the methylic salt, prepared in a sealed tube, is obtained at once in a high state of purity. These results show that, in order to obtain the best yield, the quantity of mineral acid used for the etherification must be determined for each acid separately. The advantages of dilute acid are as follows: it is easier to use, the product is more readily purified, loss of alcohol is reduced to a minimum, and compounds may be prepared which are attacked by concentrated mineral acids. J. B. T.

**Diethylacetylenic Dipropionate.** By FRANCESCO ANDERLINI (*Gazzetta*, 1895, **25**, ii, 46—57).—Klinger and Schmitz (Abstr., 1891, 890) showed that sodium acts on butyric and isovaleric chlorides, with the formation not of dibutyryl and diisovaleryl, but of dipropylacetylenic dibutyrate and diisobutyrylacetylenic diisovalerate; the reaction proceeds in the same way with propionic chloride. Sodium wire acts slowly on an ethereal solution of propionic chloride, and the ethereal liquid, on distillation, yields a yellow oil, which, after washing with sodium carbonate, drying with potassium carbonate, and distilling under reduced pressure, gives *diethylacetylenic dipropionate*, COEt·O·CEt⁚CEt·O·COEt. It is a faintly odorous, yellowish, oily liquid, which boils at 108—109° under a pressure of 10 mm., is decolorised on exposure to light, and has the densities 1·00837 at 5·6°/4° and 0·99032 at 28·1°/4°. On hydrolysis by hot alcoholic potash, it behaves in a manner analogous to its higher homologues, and yields *propyroïn*, COEt·CHEt·OH, which can be purified by distillation under reduced pressure; this boils at 132—135° under 227 mm. pressure, and has a density of 0·94288 at 16·6°/4°.

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* Heated at 100° in a sealed tube. † Methylic salt.

The densities of butyroïn and isovaleroïn are 0·9466 and 0·90256 at 16·7°/4° and 17·4°/4° respectively. Dipropylacetylenic dibutyrate has a sp. gr. = 0·94324 at 20°/4°, and diisobutylacetylenic diisovalerate a sp. gr. = 0·91320 at 20°/4°. All the above substances give normal molecular weights by the cryoscopic method. W. J. P.

**Hydroxylamidoisobutyric acid.** By Gustav Münch (*Ber.*, 1896, **29**, 62—65).—When pure acetoxime, $CMe_2{:}N{\cdot}OH$, is allowed to remain with a slight excess of anhydrous hydrogen cyanide in closed vessels at the ordinary temperature, monoclinic crystals of *hydroxylamidoisobutyronitrile*, $CN{\cdot}CMe_2{\cdot}NH{\cdot}OH$, are formed; this substance melts at 98·5°; its *hydrochloride* melts and decomposes at 210°. The best way of hydrolysing it, is to dissolve it in concentrated sulphuric acid, dilute with two-thirds as much water, and heat for a few hours at 80—85°; in this way, *hydroxylamidoisobutyric acid*,

$$COOH{\cdot}CMe_2{\cdot}NH{\cdot}OH,$$

is obtained, melting and decomposing at 168°. C. F. B.

**Optically Active Valeric acid.** By O. Schütz and Wilhelm Marckwald (*Ber.*, 1896, **29**, 52—59).—α-Methylbutyric acid, CHMeEt·COOH, was synthesised by Conrad and Bischoff's method (*Annalen*, **204**, 151), and an endeavour was made to separate it into its optically active components by fractional crystallisation of its brucine salt—the only salt amongst those tried that was at all suitable for the purpose. Even then the separation was extremely difficult; for the two optical isomerides, although hemimorphous, are not enantiomorphous, as usual, but are actually isomorphous with each other and with the inactive (racemic) salt. The *l*-acid, the brucine salt of which is the less soluble, was finally obtained with a rotation $\alpha_D = -16{\cdot}3°$ in a tube 100 mm. long, which rotation was not increased by further crystallisation, but the *d*-acid could not be obtained with a greater rotation than $\alpha_D = +10°$, and doubtless still contained some *l*-acid admixed. The brucine salts of both acids have the composition $C_5H_{10}O_2,C_{23}H_{26}N_2O_4 + 3H_2O$; that of the *l*-acid softens at 95° and melts at 100°; when anhydrous, it softens at 80° and melts at 88° to a turbid liquid, which becomes clear at 94°; that of the *d*-acid softens at 93° and melts at 95°; when anhydrous, it melts at 60—63°. The *l*-acid is like the inactive acid, in that it boils at 173—174°, does not solidify at −80°, has sp. gr. 0·954 at 0°/0°, 0·934 at 20°/4°, and 0·926 at 30°/4° (inactive, 0·936 at 20°/4°), and forms very similar salts. The calcium salt, with $5H_2O$, or $1\frac{1}{2}H_2O$ after drying in the air for two months, and the zinc salt of the *l*-acid are less soluble in hot than in cold water; 100 c.c. of an aqueous solution of the silver salt at 16°

contains 0·675 gram of the salt, whereas 100 parts of water dissolves 1·182 parts of the corresponding inactive salt at 20°. The rotation of the *l*-acid at 20° and 30° is given for light of different wavelengths.

An attempt was made to prepare from the active acid, by the action of bromine at a low temperature in the presence of phosphorus, an active acid, CBrMeEt·COOH, which would have no hydrogen atom united directly with the asymmetric carbon atom. The substance actually obtained was optically inactive, and identical with the monobromo-acid prepared by Böcking (*Annalen*, **204**, 23) by brominating inactive methylethylacetic acid at 150—160°; it is an oil, and boils at 140° under 50 mm. pressure. C. F. B.

**Action of Sulphur on Unsaturated Fatty Compounds.** By ROBERT HENRIQUES (*Zeit. angw. Chem.*, 1895, 691—692).—The author's experiments prove that a true combination of sulphur with fats or fatty acids exists. In one experiment, colza oil was fused with excess of sulphur for three hours, and after cooling, the liquid was filtered. It showed, on analysis, 3·99 per cent. of sulphur. A portion of it was now saponified with cold alcoholic soda in the presence of light petroleum, and the fatty acids were separated by hydrochloric acid. Some of the sulphur apparently existed in a free or loosely combined state, and had formed sodium sulphide, but the bulk was combined with the fatty acids, which showed 3·23 per cent. of sulphur. Treatment with hot alcoholic soda, however, removed the greater part of this sulphur, but the fatty acids still retained 1·93 per cent.

The experiment with sulphuretted linseed oil was more satisfactory. A sample, containing 8·53 per cent. of sulphur, yielded, by the cold process, fatty acids containing 6·62 per cent.; by the hot process, acids containing 5·58 per cent. of sulphur. Brown "*factis*" was next tried. A sample containing 15·48 per cent. of sulphur, gave, by the cold process, acids containing 15·20 per cent.; by the hot process, acids containing 14·14 per cent. of sulphur. L. DE K.

**Preparation of some Cobalti-Compounds.** By S. P. L. SÖRENSON (*Zeit. anorg. Chem.*, 1896, **11**, 1—5).—Potassium cobaltioxalate, $K_6Co_2(C_2O_4)_6,6H_2O$, previously obtained in small quantities by Kehrmann (Abstr., 1891, 1189), is easily prepared in the following manner: A mixture of cobalt carbonate (25 grams), a saturated solution of potassium oxalate (250 c.c.), and a saturated solution of oxalic acid (200—230 c.c.), is heated on the water bath until all the cobalt carbonate is dissolved. It is then cooled to 40°, oxidised with lead peroxide (30 grams), and then cooled and gradually mixed with acetic acid (50 c.c.), and filtered. The filtrate is precipitated, stirring constantly, with successive portions of alcohol, filtered, and the precipitate washed with absolute alcohol. The product is dissolved in the least possible quantity of water and again precipitated with alcohol. About 55—60 grams of the pure salt is obtained.

Ammonium cobaltioxalate is prepared in a similar way, but using a more concentrated solution, as the salt is much more soluble both in water and in alcohol. The author is engaged in studying the properties of these salts, and especially their behaviour towards ammonia.

E. C. R.

**Hydrolysis of the Alkyl Substitution Derivatives of Ethylic Malonate.** By EDVARD I. HJELT (*Ber.*, 1896, **29**, 110—111).—When the alkyl substitution derivatives of ethylic malonate are treated at 16° with a decinormal solution of soda in 96 per cent. alcohol, 1/20 of a gram-molecule of the compound being present per litre, it is found that, without exception, the dialkyl derivatives are much more slowly hydrolysed than the monalkyl derivatives. The rate of hydrolysis, moreover, does not appear to depend on the strength of the acid.

The experiments included ethylic malonate, together with the following derivatives: ethyl-, propyl-, isopropyl-, isobutyl-, allyl-, benzyl-, dimethyl-, diethyl-, diallyl-, and allylisopropyl-. The author considers that these phenomena are to be explained by stereochemical considerations.

A. H.

**Interconversion of Optical Antipodes.** By PAUL WALDEN (*Ber.*, 1896, **29**, 133—138).—The author has previously shown (this vol., i, 139) that asparagine can be converted into *l*-bromosuccinic acid by the action of bromine and nitrous oxide, and into *d*-bromosuccinic acid by treating the malic acid prepared from the asparagine with phosphorus pentabromide. By passing nitrous oxide into a sulphuric acid solution of aspartic acid, to which potassium bromide and bromine have been added, *l*-bromosuccinic acid separates, and may be extracted with ether. A good yield is got thus, but a practically theoretical yield of *l*-chlorosuccinic acid may be obtained by passing chlorine and nitrous oxide into a hydrochloric acid solution of aspartic acid in the cold, the acid being extracted with ether. Both lævo- and dextro-isomerides are thus obtained from the same source at the ordinary temperature.

After a number of abortive attempts, the *l*-bromosuccinic acid was converted into *l*-malic acid by warming its aqueous solution with freshly precipitated silver oxide; *d*-chlorosuccinic acid was similarly converted into *d*-malic acid. Both samples of malic acid had the proper specific rotations. It was further shown that *d*-malic acid can be converted into its *l*-isomeride in the same way that the latter can be converted into the former.

Consequently, starting with *l*-malic acid, *d*-chlorosuccinic acid can be directly prepared, and by displacing the chlorine in this by hydroxyl, *d*-malic acid, the optical isomeride of the material used, is obtained; this may then be converted into *l*-chlorosuccinic acid, which, in turn, yields *l*-malic acid again.

W. J. P.

**A Homologue of Asparagine and Derivatives of Homoaspartic acid.** By WILHELM KÖRNER and ANGELO MENOZZI (*Real. Accad. Lincei*, 1893, ii, 368—374; compare Abstr., 1890, 869).—On heating the diethylic salts of citraconic, mesaconic, and itaconic acids in sealed tubes with alcoholic ammonia at 105—110°, derivatives of the same homoaspartic acid, $COOH\cdot CMe(NH_2)\cdot CH_2\cdot COOH$, are obtained.

Ethylic citraconate, by this treatment, deposits *homoaspartic diamide*, $C_5H_{11}N_3O_2$; it crystallises in small needles melting at 175°, and when boiled with barium hydroxide, evolves ammonia and loses its alkaline reaction, yielding barium homoaspartate. The liquid from which the diamide separates contains *homoasparagine*,

$$NH_2\cdot CO\cdot CMe(NH_2)\cdot CH_2\cdot COOH,$$

which crystallises in large, efflorescent, orthorhombic plates, containing $2H_2O$, and is optically inactive; $a : b : c = 0{\cdot}695 : 1 : 2{\cdot}414$. It gives off ammonia when boiled with alkalis, and has feebly acid properties; the *copper* salt $(C_5H_9N_2O_3)_2Cu,H_2O$, crystallises in small, blue tablets, which lose water at 130—135°, becoming violet.

Diethylic mesaconate, or diethylic itaconate, when heated with alcoholic ammonia, deposits *homoaspartic monamide*, $C_5H_8N_2O_2$, which crystallises in colourless needles melting at 195°. On boiling with barium hydroxide, ammonia is evolved, and a barium salt is formed, from which *homoaspartic acid* may be obtained; it crystallises in transparent, hemihedral, orthorhombic prisms with $1H_2O$, and, when anhydrous, melts at 166·5—167°; $a : b : c = 0{\cdot}658 : 1 : 1{\cdot}211$. The solution is optically inactive, but the crystals are hemihedrally developed, so that the two active isomerides may be separated.

W. J. P.

**Preparation of αα-Dimethylglutaric acid from the Corresponding Hydroxy-acid.** By SERGIUS REFORMATSKY (*Ber.*, 1895, **28**, 3262—3265; compare this vol., i, 128).—*β-Hydroxy-αα-dimethylglutaric acid*, $COOH\cdot CHMe\cdot CH(OH)\cdot CHMe\cdot COOH$, is prepared by the action of ethylic bromopropionate and ethylic formate on zinc; it crystallises in needles, and melts at 135—136°, but the liquid only becomes transparent at 141°. The electrolytic conductivity $k = 0{\cdot}0108$, $\mu\infty = 350$. The *ethylic salt* is oily, almost colourless, boils at 270—271°, and is most readily converted into the acid by means of barium hydroxide. The *anhydride* melts at 108—109°, and is crystalline. A *calcium* salt has also been prepared. When reduced by means of hydriodic acid, the hydroxy-acid is converted into fumaroïd αα-dimethylglutaric acid, but it melts at 145—145·5°, not at 140—141°, as stated by Auwers (Abstr., 1895, i, 209), no maleïnoid acid is formed. Auwers (*loc. cit.*) referred the production of this isomeride by Zelinsky's method, to the fact that it is prepared from ethylic α-cyanopropionate, which contains an asymmetric carbon atom; as ethylic α-bromopropionate also contains one, this view requires modification.

J. B. T.

**Reactions of Tartaric acid and Alkali Tartrates.** By LOUIS MAGNIER DE LA SOURCE (*Compt. rend.*, 1895, **121**, 774—776).—Potassium hydrogen tartrate is readily soluble in a concentrated solution of potassium acetate, and hence a small quantity of tartaric acid added to such a solution produces no precipitate. Precipitation, however, takes place at once if acetic acid is added, and is also accelerated by the addition of alcohol and ether. Acetic acid partially decomposes alkali tartrates if a mixture of the two is allowed to evaporate, and conversely, a hydrogen tartrate partially decomposes an alkali acetate. The residue left after spontaneous evaporation is a mixture of normal tartrate, acetate, and hydrogen tartrate. A mixture of 1 mol. of tartaric acid and 2 mols. each of acetic acid and normal alkali tartrate, loses 95 per cent. of the acetic acid on spontaneous evaporation, and this is increased to 97 or 97·5 per cent. when the proportion of tartaric acid is doubled or trebled.

Calcium sulphate decomposes normal alkali tartrates completely, but hydrogen tartrates only incompletely, whether in presence of water or dilute alcohol. Its action on normal tartrates is not affected by the presence of potassium acetate, but its action on the hydrogen tartrates ceases to be limited in presence of the acetate.

Tartaric acid partially displaces sulphuric acid from potassium sulphate, and hydrochloric acid from potassium chloride, these acids being partially expelled when the solution is evaporated to dryness and heated. Under similar conditions, however, sodium chloride loses only a minute quantity of hydrochloric acid. C. H. B.

**Easy Method of Preparing Lævorotatory Tartaric acid.** By WILHELM MARCKWALD (*Ber.*, 1896, **29**, 42—43).—A boiling aqueous solution of racemic acid is treated with half the cinchonine necessary to form the acid salt, and water is added until a clear solution is obtained, which is then allowed to cool; after remaining for a day, the cinchonine *l*-tartrate, which has crystallised out, is filtered off. The mother liquor deposits the *d*-tartrate, which is filtered off after two days; this second mother liquor is divided into two halves, and these are neutralised, the one with sodium hydroxide, the other with ammonia, filtered from precipitated cinchonine, mixed, and concentrated; sodium ammonium *d*-tartrate crystallises out on cooling, and this crystallisation is allowed to go on until the mother liquor has become inactive or feebly lævorotatory. The last mother liquor is worked up for racemic acid, which can be used over again, and the *d*- and *l*-tartrates obtained above are converted into the corresponding acids in the usual way. C. F. B.

**Nitrocarbamide, Nitro-urethane, and Nitramide.** By JOHANNES THIELE and ARTHUR LACHMAN (*Annalen*, 1895, **288**, 267—311; compare Abstr., 1894, i, 399).—Nitrocarbamide is strongly acidic, liberating acetic acid from its salts. The *potassium* derivative is readily soluble in water, and the *silver* derivative crystallises in minute prisms dissolving readily in nitric acid and ammonia; the *mercury* derivative is very soluble in hydrochloric acid, dissolving with difficulty in nitric and sulphuric acids, and it yields nitrocarbamide when treated with ammonium sulphide.

*Nitroethylcarbamide*, $NO_2{\cdot}NH{\cdot}CO{\cdot}NHEt$, is obtained by adding ethylic nitrate to a solution of ethylcarbamide in sulphuric acid; it crystallises from ether in long needles and melts at 130—131°. It dissolves readily in hot water, and is sparingly soluble in cold; hydrolysis with potash gives rise to ethylamine. The *ammonium* and *potassium* derivatives are hygroscopic; the *silver* derivative crystallises in white leaflets.

Nitro-urethane (*loc. cit.*) is prepared by treating a solution of urethane in sulphuric acid with ethylic nitrate at 0°; it decomposes at 140°. The *potassium* derivative crystallises from water in large, rhombic prisms, and the *mercury* derivative is a white powder dissolving readily in hydrochloric acid; the *silver* derivative crystallises in aggregates of minute needles, and with methylic iodide yields nitromethylurethane (compare Abstr., 1895, i, 445).

*Ethylic benzylidenehydrazinecarboxylate*, $CHPh{:}N{\cdot}NH{\cdot}COOEt$, is obtained by reducing nitro-urethane and agitating the product with benzaldehyde; it crystallises from dilute alcohol in long needles melting at 135—136°, and the *potassium* derivative is unstable in aqueous solution. The *hydrochloride* of ethylic hydrazinecarboxylate is obtained from the benzylidene derivative by the action of warm hydrochloric acid; it is readily soluble in water and alcohol, and separates in yellowish leaflets on adding ether to the solution in methylic alcohol.

The *mercury* derivative of nitramide (Abstr., 1894, ii, 412) is an unstable substance dissolving readily in hydrochloric, but only sparingly in nitric acid; the action of hot water gives rise to red mercuric oxide.

*Nitrosocarbamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}NO$, is obtained in solution when nitrocarbamide is reduced with zinc dust and caustic soda; the liquid develops an intense purple coloration with ferrous sulphate, and effervesces above 0°.

*Nitroso-urethane*, $NO{\cdot}NH{\cdot}COOEt$, is produced on reducing the ammonium derivative of nitro-urethane with zinc dust and acetic acid; it crystallises from petroleum in beautiful needles, and melts and decomposes completely at 51—52°, yielding aldehyde. It gives Liebermann's reaction, and does not develop a colour with ferrous sulphate and caustic soda; the aqueous solution effervesces vigorously when treated with acids or alkalis, yielding ethylic alcohol, carbonic anhydride, and nitrogen. The *silver* derivative is yellow, and explodes when heated; the *potassium* derivative crystallises in yellow needles, and the *ammonium* derivative in yellow leaflets. Potassium permanganate oxidises nitroso-urethane to nitro-urethane, and ammonia converts it into urethane, whilst aniline gives rise to phenylurethane.

*Potassium nitrosocarbamate*, $NO{\cdot}NK{\cdot}COOK$, is obtained from nitroso-urethane by the action of potash dissolved in methylic alcohol; it is a yellow powder, which explodes violently when brought in contact with water, but is perfectly stable in dry air. M. O. F.

**Preparation of Semicarbazide.** By JOHANNES THIELE and CARL HEUSER (*Annalen*, 1895, **288**, 311—313).—The unstable character of nitrosocarbamide seriously diminishes the yield of semicarbazide obtained by the reduction of nitrocarbamide; under conditions which lead to the immediate reduction of nitrosocarbamide, however, 50 per cent. of the quantity required by theory may be obtained.

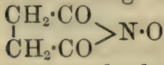
The *zinc chloride compound* of acetone-semicarbazone,

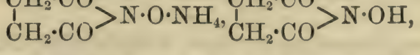
$$(CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2)_2,ZnCl_2,$$

is obtained by adding sodium acetate and acetone to nitrosocarbamide reduced in acetic acid solution by means of zinc dust mixed with powdered ice; it crystallises from water in slender needles, and melts and decomposes at 196°. Ammonia converts the substance into acetonesemicarbazone, which may then be employed as a source of semicarbazide. M. O. F.

**Cyanuric acid from Hydroxyoxamide.** By HUGO SCHIFF and U. MONSACCHI (*Annalen*, 1895, **288**, 313—318, and *Gaz.*, **25**, ii, 446—450).—*Hydroxyloxamide*, $OH\cdot NH\cdot CO\cdot CO\cdot NH_2$, is obtained by the action of hydroxylamine on ethylic oxamate, and appears to be identical with oximamidoxalic acid, $NH_2\cdot C(NOH)\cdot COOH$, described by Holleman (Abstr., 1894, i, 571); the aqueous solution develops an intense red coloration with ferric chloride. *Acetoxyoxamide*, $OAc\cdot NH\cdot CO\cdot CO\cdot NH_2$, is obtained by the action of acetic anhydride on the foregoing compound, and crystallises in nacreous leaflets melting at 172—174°; the substance is indifferent towards ferric chloride, and, when heated at 100—110° with acetic anhydride, gives rise to cyanuric acid, an intermediate *compound*, melting at 218°, being also formed.

*Phenylhydroxyloxamide*, $OH\cdot NH\cdot CO\cdot CO\cdot NHPh$, is formed when ethylic phenyloxamate is hydrolysed with alcoholic hydroxylamine; it crystallises in leaflets and melts at 159°. The *acetyl* derivative melts at 182—183°, and does not yield cyanuric acid. M. O. F.

**Action of Hydroxylamine on Succinic Anhydride.** By GIORGIO ERRERA (*Gazzetta*, 1895, ii, 25—37).—On adding succinic anhydride to an alcoholic solution of hydroxylamine, *hydroxylamine succinylhydroxamic acid* separates as a semi-solid mass. On mixing the anhydride with an alcoholic solution of hydroxylamine and sodium ethoxide, and adding ammonia and barium chloride, the *barium* salt, $(C_4H_6NO_4)_2Ba$, of succinylhydroxamic acid is obtained; it crystallises in small, colourless prisms, and gives a violet colour with ferric chloride; the *hydrogen barium* salt, $C_4H_5NO_2Ba,4H_2O$, crystallises in laminæ. *Succinylhydroxamic acid*, $OH\cdot C(NOH)\cdot CH_2\cdot CH_2\cdot COOH$, can be obtained from these salts as a deliquescent, viscous liquid; on heating with acetic chloride, it yields *succinylacetoxylamine*,  $\begin{array}{l}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{array}\!\!>N\cdot OAc$, which separates from benzene in lustrous, colourless, orthorhombic crystals melting at 129—130°; $a : b : c = 0{\cdot}99826 : 1 : 0{\cdot}45945$. On crystallisation from hot water, it undergoes partial hydrolysis yielding a syrupy solution from which *succinylhydroxylamine* crystallises when the latter is evaporated over sulphuric acid. On adding alcoholic ammonia to the alcoholic solution of this amine or its acetyl derivative, an *ammonium* compound,

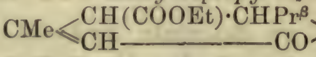


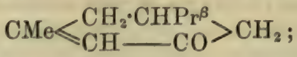
$$\begin{array}{l}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{array}\!\!>N\cdot O\cdot NH_4,\begin{array}{l}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{array}\!\!>N\cdot OH,$$

is deposited; it crystallises in colourless, monoclinic prisms, melts and decomposes at 175°, and is very soluble in water. On boiling with soda, it yields succinylhydroxamic acid. W. J. P.

**The Hexamethylene Series. Synthesis of Nononaphthene.** By NICOLAI D. ZELINSKY and A. REFORMATZKY (*Ber.*, 1896, **29**, 214—216).—Trimethylhexamethylene alcohol, prepared synthetically from trimethylpimelic acid (this vol., i, 130), yields, when reduced, a saturated hydrocarbon, $C_9H_{18}$, which boils at 142—144°, has a sp. gr. = 0·7807 at 18°/4°, and yields tribromopseudocumene when treated with bromine in the presence of aluminium bromide. This hydrocarbon, 1 : 2 : 5-trimethylhexamethylene, is thus nothing else than hexahydropseudocumene; it may be regarded as a synthetical nononaphthene. The nononaphthene, obtained from Caucasian naphtha by Markownikoff and Oglobin and by Konowaloff, is probably a mixture containing some hexahydropseudocumene; only 7 per cent. of it can be converted into tribromopseudocumene. C. F. B.

**1 : 5-Diketones.** By EMIL KNOEVENAGEL (*Annalen*, 1895, **288**, 321—360; compare Abstr., 1893, i, 419, and 1895, i, 48).—Ethylic isobutylidenediacetoacetate, $CHPr^{\beta}(CHAc{\cdot}COOEt)_2$, is obtained by adding diethylamine or piperidine (1 gram) to a mixture of ethylic acetoacetate (100 grams) and isobutylaldehyde (28 grams) cooled at 0°, four equal quantities of the base being subsequently added at intervals of 10 to 12 hours, while the temperature of the liquid is maintained between 0° and −10°; it forms lustrous, colourless crystals, and melts at 117°.

*Ethylic* 3 : 5-*methylisopropyl*-$\Delta_2$-*ketotetrahydrobenzene*-4 : 6-*dicarboxylate*,  $\mathrm{CMe}{<}\begin{matrix}\mathrm{CH(COOEt){\cdot}CHPr^{\beta}}\\ \mathrm{CH}\text{————————}\mathrm{CO}\end{matrix}{>}\mathrm{CH{\cdot}COOEt}$, is produced when acids and alkalis act on the foregoing substance; distillation gives rise to isomeric ethylic 3 : 5-methylisopropyl-$\Delta_2$-ketotetrahydrobenzenemonocarboxylates, the mixture forming a pale yellow oil, which boils at 170° under a pressure of 17 mm. (compare Hagemann, Abstr., 1893, i, 393). *Ethylic* 3 : 5-*methylisopropyl*-$\Delta_2$-*ketotetrahydrobenzene*-4-*carboxylate* is isolated from this mixture by means of its insolubility in caustic soda; it boils at 161° and 170° under pressures of 11 mm. and 17 mm. respectively, and the alcoholic solution is indifferent towards ferric chloride. *Ethylic* 3 : 5-*methylisopropyl*-$\Delta_2$-*ketotetrahydrobenzene*-6-*carboxylate* is soluble in caustic soda; it boils at 166° and 170° under pressures of 14 mm. and 17 mm. respectively, and develops an intense reddish-violet coloration with ferric chloride. Hydrolysis of these two ethylic salts converts them into the corresponding *acids*, which spontaneously lose carbonic anhydride, yielding 3 : 5-*methylisopropyl*-$\Delta_2$-*ketotetrahydrobenzene*, or metacamphor,



$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CH_2{\cdot}CHPr^{\beta}}\\ \mathrm{CH}\text{——}\mathrm{CO}\end{matrix}{>}\mathrm{CH_2};$$

this substance is also formed when ethylic isobutylidenediacetoacetate is heated for two hours at 110° (compare Abstr., 1893, i, 419, and 1894, i, 575).

*Ethylic isovalerylidenediacetoacetate*, $CH_2Pr^{\beta}{\cdot}CH(CHAc{\cdot}COOEt)_2$, is obtained from ethylic acetoacetate and isovaleraldehyde by means of piperidine or diethylamine; it crystallises from dilute alcohol, and melts at 134—135°. When heated with water for five hours in a reflux apparatus, it yields *ethylic* 3 : 5-*methylisobutyl*-$\Delta_2$-*ketotetrahydrobenzene*-4 : 6-*dicarboxylate*, a colourless liquid, which boils at 186—188° under a pressure of 20 mm.; the *oxime* crystallises in small, white needles, which melt at 108—109°, and yields a *benzoyl* derivative, crystallising from dilute alcohol in leaflets, and melting at 157—158°. When ethylic 3 : 5-methylisobutyl-$\Delta_2$-ketotetrahydrobenzene-4 : 6-dicarboxylate is hydrolysed with 20 per cent. sulphuric acid, a mixture of ethylic salts is obtained, boiling at 167—169° under a pressure of 20 mm., and these are separated by the method adopted for the isopropylic derivatives. *Ethylic* 3 : 5-*methylisobutyl*-$\Delta_2$-*ketotetrahydrobenzene*-6-*carboxylate* forms a *phenylhydrazone*, which crystallises from alcohol in small, white needles, and melts at 162—163°. *Ethylic* 3 : 5-*methylisobutyl*-$\Delta_2$-*ketotetrahydrobenzene*-4-*carboxylate* yields an *oxime*, which melts at 101—103°, and gives rise to a *benzoyl* derivative melting at 146—148°.

3 : 5-*Methylisobutyl*-$\Delta_2$-*ketotetrahydrobenzene* is produced when ethylic isovalerylidenediacetoacetate is heated with alcoholic potash for 2—3 hours, and it is also obtained by hydrolysing the foregoing ethylic mono- and di-carboxylates; the ketone has an agreeable odour, and boils at 146—148° and 130° under pressures of 22 mm. and 10 mm. respectively. The *oxime* crystallises in colourless needles, melting at 92—94°, and gives rise to a *benzoyl* derivative, which crystallises in lustrous leaflets, and melts at 138—140°. The *phenylhydrazone* crystallises from alcohol in silky needles, and melts at 149—151°.

3 : 5-*Methylisobutylphenol* is obtained by adding bromine to a solution of the ketone in carbon bisulphide, and, after removing the solvent, heating the product at 120°; it boils at 142—144° under a pressure of 20 mm., and is indifferent towards ferric chloride. The *tribromo*-derivative, $C_{11}H_{13}OBr_3$, crystallises in white needles, and melts at 128—130°.

*Ethylic oenanthylidenediacetoacetate*,

$$CH_2Me\cdot[CH_2]_4\cdot CH(CHAc\cdot COOEt)_2,$$

crystallises from petroleum in white, lustrous needles, and melts at 71°; it is readily converted into *ethylic* 3 : 5-*methylhexyl*-$\Delta_2$-*ketotetrahydrobenzene*-4 : 6-*dicarboxylate*, which boils at 195—196° and 202—204° under pressures of 9 mm. and 17 mm. respectively. The *oxime* of the latter ethylic salt is produced when hydroxylamine acts on the former; it melts at 116—118°, and yields a *benzoyl* derivative, which crystallises in colourless, lustrous leaflets, and melts at 165—166°.

*Ethylic* 3 : 5-*methylhexyl*-$\Delta_2$-*ketotetrahydrobenzene*-4-*carboxylate* is separated by means of its insolubility in caustic soda from the mixture of isomerides obtained on hydrolysing the foregoing ethylic dicarboxylates; it is indifferent towards ferric chloride, and yields an *oxime* melting at 109—111°, which gives rise to a *benzoyl* derivative, melting at 157—159°. *Ethylic* 3 : 5-*methylhexyl*-$\Delta_2$-*ketotetrahydrobenzene*-6-*carboxylate* is also separated from the mixture, which boils at 186—188° under a pressure of 18 mm.; it develops a dark violet coloration with ferric chloride, and yields a *phenylhydrazone*, which crystallises in orange-yellow needles, and melts at 146—147°.

3 : 5-*Methylhexyl-$\Delta_2$-ketotetrahydrobenzene* is the final product arising from hydrolysis of the foregoing ethylic salts; it has a bitter taste and agreeable odour, and boils at 166—168° under a pressure of 22 mm. The *oxime* melts at 103—105°, and yields a *benzoyl* derivative, which crystallises in white, lustrous leaflets, and melts at 150—152°. The *phenylhydrazone* crystallises in silky needles, and melts at 157—159°.

3 : 5-*Methylhexylphenol* boils at 160—162° under a pressure of 18 mm., and is indifferent towards ferric chloride; the *tribromo*-derivative, $C_{13}H_{17}OBr_3$, melts at 137—139°.

*Ethylic benzylidenebisacetonedicarboxylate*,

$$CHPh[CH(COOEt)\cdot CO\cdot CH_2\cdot COOEt]_2,$$

is obtained by the action of benzaldehyde on ethylic acetonedicarboxylate, employing diethylamine, piperidine, or ammonia as the condensing agent; it crystallises from alcohol in white, silky needles, and melts at 146°. Although water is eliminated very readily, an individual ketotetrahydrobenzene derivative has not been isolated by distillation; successive treatment with sodium ethoxide and aqueous potash, however, converts it into 3 : 5-methylphenyl-$\Delta_2$-ketotetrahydrobenzene (Abstr., 1895, i, 50).

*Ethylic methylenebisacetonedicarboxylate*,

$$CH_2[CH(COOEt)\cdot CO\cdot CH_2\cdot COOEt]_2,$$

is prepared from formaldehyde and ethylic acetonedicarboxylate, diethylamine being used as the condensing agent; it melts at 105°. Hydrolysis converts it into 3-methyl-$\Delta_2$-ketotetrahydrobenzene, identical with the substance obtained on hydrolysing ethylic 3-methyl-$\Delta_2$-ketotetrahydrobenzene-4 : 6-dicarboxylate (*loc. cit.*).

*Ethylic ethylidenebisacetonedicarboxylate*,

$$CHMe[CH(COOEt)\cdot CO\cdot CH_2\cdot COOEt]_2,$$

obtained from acetaldehyde, ethylic acetonedicarboxylate, and diethylamine, crystallises in white, silky needles, and melts at 115°; hydrolysis with 20 per cent. sulphuric acid converts it into 3 : 5-dimethyl-$\Delta_2$-ketotetrahydrobenzene.

*Ethylic isobutylidenebisacetonedicarboxylate*,

$$CHPr^{\beta}[CH(COOEt)\cdot CO\cdot CH_2\cdot COOEt]_2,$$

melts at 104°; on hydrolysis, it yields 3 : 5-methylisopropyl-$\Delta_2$-ketotetrahydrobenzene. *Ethylic isovalerylidenebisacetonedicarboxylate* melts at 118°, and yields 3 : 5-methylisobutyl-$\Delta_2$-ketotetrahydrobenzene when hydrolysed. *Ethylic oenanthylidenebisacetonedicarboxylate* melts at 125°, and yields 3 : 5-methylhexyl-$\Delta_2$-ketotetrahydrobenzene on hydrolysis. M. O. F.

**Derivatives of Chlorodihydrobenzene.** By CH. GUNDLICH and EMIL KNOEVENAGEL (*Ber.*, 1896, **29**, 169—171; compare Abstr., 1895, i, 86 and 654).—When 1 : 3-methylisopropylcyclohexanone (3 : 5-methylisopropyl-$\Delta_2$-ketotetrahydrobenzene) is treated in chloroform solution with phosphorus pentachloride, hydrogen chloride is given off, and 5-*chlorodihydrometacymene* (1 : 3 : 5-methylisopropylchlorocyclohexadiene) is formed. This distils over at 106° under a pressure of 15 mm.

as a colourless, limpid oil; it is transformed back into the ketone by the action of 95 per cent. sulphuric acid. On treatment with bromine and quinoline, it yields 5-*chlorometacymene*, which distils under atmospheric pressure at 222—223°.

5 : 2 : 4 : 6-*Chlorotrinitrometacymene*, obtained by the action of nitric acid on the preceding compound, forms colourless crystals, melts at 124—125°, sublimes on heating, and smells intensely of musk.

The trinitro-compound, with aniline, yields 2 : 4 : 6 : 5-*trinitroanilidometacymene*, which melts at 155°; whilst with alcoholic ammonia it yields 2 : 4 : 6-*trinitro*-1 : 3 : 5-*cymidine*, which melts at 103—104°.

5-*Chlorodihydrometaisobutyltoluene* (1 : 3 : 5-methylisobutylchlorocyclohexadiene) is obtained by the action of phosphorus pentachloride on methylisobutylcyclohexanon (*Annalen*, **288**, 336). It is a strongly refractive liquid, and distils at 113—115° under a pressure of 15 mm. When treated with bromine or quinoline, it yields 5-*chlorometaisobutyltoluene*, which distils under atmospheric pressure at 234—235°.

5-*Chlorometahexyldihydrotoluene* (1 : 3 : 5-methylhexylchlorocyclohexadiene) boils at 148—150° under a pressure of 25 mm., and with bromine and quinoline yields 5-*chlorometahexyltoluene*, which distils under atmospheric pressure at 273—275°. J. J. S.

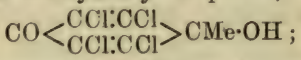
**The Benzene Problem.** By VICTOR MEYER (*Ber.*, 1895, 3195—3196).—This is a reply to criticisms by Brühl (this vol., i, 147) on the paper by Heyl and V. Meyer (*ibid.*, 145). As regards the question of priority between Brühl and Wegscheider (Abstr., 1895, i, 593, and 449) concerning the hydrolysis of ethereal salts, the author points out that Conrad and Brückner were the first to draw attention to the rules regulating the hydrolysis, and to compare the results of hydrolysis with those of etherification. J. J. S.

**The Benzene Nucleus.** By WILHELM VAUBEL (*J. pr. Chem.*, 1895, [2], **52**, 548—555).—The author shows that his configuration for benzene (Abstr., 1894, i, 325) is in accord with the following facts. (1) Metanitraniline hydrochloride is the most stable of the nitraniline hydrochlorides (Lellmann, Abstr., 1885, 251). (2) Ammonia reacts with ortho- and para-bromonitrobenzene to form nitranilines, but not with metabromonitrobenzene (Schöpff, Abstr., 1892, 335; P. Fischer, *ibid.*, 331; Lobry de Bruyn, Abstr., 1891, 428). (3) Ortho- and para-nitraniline react with ammonia to form the corresponding nitrophenols; metanitraniline does not so react. (4) Ammonia reacts with ortho- and para-nitranisoïl to form the corresponding nitranilines, but not with metanitranisoïl. (5) Of the nitranilines the meta-compound combines most readily with phenylthiocarbimide. (6) Ortho- and para-xylene are readily oxidised to the corresponding toluic acids, metaxylene far less readily. (7) Hydrochloric acid at high temperatures converts ortho- and parahydroxybenzoic acids into phenol, but not the meta-acid. (8) Of the nitrobenzaldehydes, the meta-compound is more easily oxidised by nitric acid than is the ortho-compound. (9) Metahydroxybenzoic acid is reduced to the corresponding alcohol by sodium amalgam, in which respect it differs from both its isomerides.

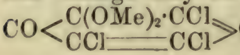
In the same connection, the author quotes Sudborough on the substituted benzoic chlorides and the hydrolysis of nitriles and amides (Trans., 1895, 587, 601). Some speculations concerning the manner in which naphthalene tetrachloride yields four dichloronaphthalenes according to the treatment to which it is subjected, conclude the paper. A. G. B.

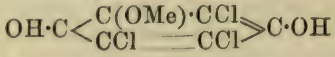
**4 : 3 : 5-Bromodinitrotoluene and its Derivatives.** By C. Loring Jackson and M. H. Ittner (*Ber.*, 1895, **28**, 3063—3066).—This substance was prepared by the diazo-reaction from the corresponding 4-amido-compound; it forms yellowish prisms, and melts at 118°; with aniline it yields, in the cold, 3 : 5 : 4-*dinitranilidotoluene*, which is orange-yellow and melts at 169°. The bromo-compound does not react with ethylic sodiomalonate, and is oxidised only with difficulty, dichromate and sulphuric acid converting it into 4 : 3 : 5-*bromodinitrobenzoic acid*. This forms colourless plates, and melts at 181°; the bromine atom in it is much more easily replaced than in the case of the preceding compound; on warming with ammonia, it is converted into the 4-amido-compound (chrysanisic acid); with aniline, it yields the orange-yellow 3 : 5 : 4-*dinitroanilidobenzoic* acid melting at 236°, and with ethylic sodiomalonate, it gives *ethylic* 2 : 6 : 4-*dinitrocarboxyphenylmalonate*, $\mathrm{COOH{\cdot}C_6H_2(NO_2)_2{\cdot}CH(COOEt)_2}$, which melts at 176°. With most of these substances sodium ethoxide forms unstable coloured substances, possibly adding itself on to the nitro-groups; certainly the other groups are not displaced. C. F. B.

**New Series of Quinonoïd Derivatives.** By Theodor Zincke (*Ber.*, 1895, **28**, 3121—3127).—When tetrachloroparacresol is oxidised with nitric acid, a single atom of oxygen is taken up, giving rise to the formation of the hydroxy-compound,



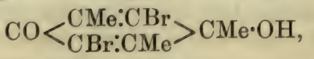
$$\mathrm{CO}{<}\begin{smallmatrix}\mathrm{CCl{:}CCl}\\ \mathrm{CCl{:}CCl}\end{smallmatrix}{>}\mathrm{CMe{\cdot}OH}\,;$$

this change may be compared with the conversion of the ketone  $\mathrm{CO}{<}\begin{smallmatrix}\mathrm{C(OMe)_2{\cdot}CCl}\\ \mathrm{CCl{=\!=}CCl}\end{smallmatrix}{\geqslant}\mathrm{C{\cdot}OH}$ into the dihydroxy-compound

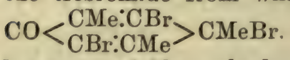


$$\mathrm{OH{\cdot}C}{<}\begin{smallmatrix}\mathrm{C(OMe){\cdot}CCl}\\ \mathrm{CCl{=\!=}CCl}\end{smallmatrix}{\geqslant}\mathrm{C{\cdot}OH}$$

(Abstr., 1894, i, 232). It is probable that hydroxydibromopseudocumenol (Auwers, this vol., i, 151) is a member of the new class of derivatives, being represented by the formula



$$\mathrm{CO}{<}\begin{smallmatrix}\mathrm{CMe{:}CBr}\\ \mathrm{CBr{:}CMe}\end{smallmatrix}{>}\mathrm{CMe{\cdot}OH},$$

the tribromide from which it is obtained having the constitution  $\mathrm{CO}{<}\begin{smallmatrix}\mathrm{CMe{:}CBr}\\ \mathrm{CBr{:}CMe}\end{smallmatrix}{>}\mathrm{CMeBr}$. Oxidation of dibromopseudocumenol, however, yields a hydroxy-derivative which is isomeric and not identical with the compound described by Auwers. M. O. F.

**Preparation of Trichlorotoluquinone.** By Karl Elbs and E. Brunnschweiler (*J. pr. Chem.*, 1895, [2], **52**, 559—560).—20 grams of orthotoluidine is dissolved in the necessary quantity of dilute hydrochloric acid, and 700 c.c. of crude concentrated hydrochloric acid is added, and, in the course of an hour, 190 grams of dry, powdered sodium dichromate are added. The temperature is kept below 30—40°, and, after two hours, the mixture is heated for half an hour on the water bath, then diluted with a litre of water and filtered. The contents of the filter are washed into a flask with a little strong hydrochloric acid, and heated for an hour on the water bath; water is again added, the whole is filtered, and the solid once more washed with dilute hydrochloric acid into the flask. Several grams of dichromate are now added, and, after warming for a quarter of an hour, the solid matter is filtered and washed. After two treatments with alcohol, the residual dirty yellow powder is crystallised from benzene. In this way, 20 grams of toluidine yield 16—17 grams of trichlorotoluquinone. Aniline may be similarly converted into chloranil. A. G. B.

**Synthesis and Constitution of Eugenol.** By CHARLES MOUREAU (*Compt. rend.*, 1895, **121**, 721—723).—The action of allylic iodide on dimethylcathechol (veratrol), $C_6H_4(OMe)_2$, yields methyleugenol identical in physical and chemical properties with the natural product. Some methylic iodide, catechol, and guaiacol are formed at the same time. The methyleugenol, when boiled with alcoholic potash, is converted into isomethyleugenol; with chromic mixture, it yields methylvanillin and methylvanillic acid, and with potassium permanganate, it yields the same acid [COOH : OMe : OH = 1 : 3 : 4]. These results confirm the constitution generally ascribed to eugenol. C. H. B.

**Orthonitrobenzylic Mercaptan.** By SIEGMUND GABRIEL and ROB. STELZNER (*Ber.*, 1896, **29**, 160—165; compare Abstr., 1895, 432).—Orthonitrobenzylic carbaminthiolate,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}CO{\cdot}NH_2,$$

when boiled with 10 times its weight of 20 per cent. hydrochloric acid, yields *orthonitrobenzylic hydrosulphide*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}SH$, together with a small quantity of orthonitrobenzylic sulphide; the former may be separated by steam distillation, as it is readily volatile. By exposing a concentrated solution of the mercaptan in methylic alcohol to low temperatures, it is obtained in long, yellow needles, which have a characteristic odour, and melt at 42—44°. The author thinks that his compound is identical with Jahoda's nitrobenzylic bisulphide (m. p. 47°) (Abstr., 1890, 487), since the true bisulphide, according to Cassirer (Abstr., 1893, 16), melts at 112—113°. This bisulphide may easily be obtained from the hydrosulphide by treatment with a solution of iodine. The hydrosulphide, when treated with a 33 per cent. solution of potassium hydroxide, yields phenoisothiazole and nitrobenzylic bisulphide; zinc chloride also gives the same thiazole.

*Methylic orthonitrobenzylic sulphide*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}SMe$, is obtained by dissolving the hydrosulphide in methylic alcohol, and treating the mixture with sodium methoxide and methylic iodide; it is a thick, yellowish oil, and, on heating it with methylic iodide at 100°, is decomposed, yielding nitrobenzylic iodide, trimethylsulphine iodide, and a third substance which melts at 67—70°.

*Methylic orthoamidobenzylic sulphide*, obtained by the action of zinc dust and acetic acid on the nitro-compound, is a colourless oil, which boils at 277—278°, and does not solidify at −18°. The *hydrochloride* crystallises in long, colourless needles; its acetyl derivative, $NHAc\cdot C_7H_6\cdot SMe$, melts at 102°, and its benzoyl derivative at 118°.

J. J. S.

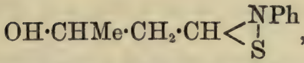
**Action of Hypobromous acid and Hypochlorous acid on Acid Anilides.** By E. E. Slosson (*Ber.*, 1895, **28**, 3265—3270).—*Acetobromamidobenzene*, NBrPhAc, mixed with acetoparabromanilide, is obtained by the action of alkaline hypobromite solution on acetanilide at 0°; the liquid is acidified with boric acid, when the compound is deposited in rectangular, yellowish plates, melting at 75—80°. It is unstable, and in presence of moisture is converted into acetoparabromanilide; the change is instantaneous at its melting point or when it is boiled with water; it liberates iodine from potassium iodide and nitrogen from ammonia, and in stability is midway between the corresponding chloro- and iodo-derivatives. *Formobromamidobenzene*, HCO·NPhBr, resembles the preceding compound in general properties, and is formed in a similar manner from formanilide; it is deposited in yellow crystals melting at 55—57°. The above preparations contained about 10 and 20 per cent. respectively of the parabromanilides. Sodium hypochlorite gives a better yield of acetochloramidobenzene than bleaching powder and hydrochloric acid; it was therefore employed in the preparation of the compounds described below. *Formochloramidobenzene*,

HCO·NPhCl,

crystallises from ether or dilute acetic acid in colourless plates, melts at 43—44°, is not reduced to formanilide by the action of ammonia, hydriodic acid, or alcohol, and is not changed when heated alone at 100°. *Formoparachloranilide*, $HCO\cdot NH\cdot C_6H_4Cl$, is prepared by heating the preceding compound with hydrochloric acid, or from parachloraniline and formic acid, and is deposited in colourless crystals melting at 101°. *Benzochloramidobenzene*, NClPhBz, crystallises from light petroleum in needles melting at 78—80°.

The action of an alkali does not cause intramolecular rearrangement (exchange of position between the haloïd and radicle; Beckmann's reaction) in any of the above haloïd amides, although compounds of the analogous type RCO·NHX (X = Cl or Br) react in this manner with the greatest readiness; the cause of this difference in behaviour is being investigated.

J. B. T.

**Thioaldolaniline and Aldehyde-green.** By Wilhelm von Miller and Josef Plöchl (*Ber.*, 1896, **29**, 59—61).—Recognising that substances containing the group >C:N– readily form additive products, the authors thought it possible that this group might directly take up hydrogen sulphide or sulphur. As a matter of fact, aldolanilide, $OH\cdot CHMe\cdot CH_2\cdot CH{:}NPh$ (Abstr., 1894, i, 414), could not be made to unite simply with hydrogen sulphide; but, by heating it in absolute alcoholic solution with crystallised ammonium sulphide, a white substance,  $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH<\overset{NPh}{\underset{S}{|}}$, was obtained; this melts at 92°, and turns yellowish when kept for a time. The sulphur in aldehyde-green doubtless exists therein combined in much the same fashion. C. F. B.

**Thiodiazo-derivatives.** By ARTHUR R. HANTZSCH and HANS FREESE (*Ber.*, 1895, **28**, 3237—3251).—The thiodiazo-derivatives described below were all prepared by the action of phenylic hydrosulphide on diazonium salts in alkaline solution. The diazo-ethers, RN:NOR, are now generally recognised as iso-derivatives, and these are probably "anti" compounds, but as all efforts to prepare "syn" isomerides have been unsuccessful, this is not absolutely proved. The thio-ethers are more stable than the oxy-ethers, and do not combine with naphthols either in alkaline or alcoholic solution; they are also probably "anti" compounds, but attempts to prepare isomerides were unsuccessful. The slow combination of naphthol and diazosulphanilic acid thio-ether is probably caused by the regeneration, under the influence of water, of some diazosulphanilic acid. The diazo-ethers are yellow and stable at 0°; alkalis and dilute acids are without action on them; with concentrated acids, their components are regenerated; they form unstable additive products with hydrogen chloride, and, when heated, explode and yield nitrogen; when warmed with water, nitrogen and a sulphide, RSPh, are formed, but hydrolysis also occurs, and consequently a phenol and phenylic hydrosulphide, or its oxidation product, phenylic bisulphide, are also produced.

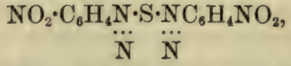
*Diazobenzenethiophenyl ether*, PhN:N·SPh, prepared from phenylic hydrosulphide and diazonium chloride at −5°, is oily and unstable. *Antiparachlorodiazobenzenethiophenyl ether*, $C_6H_4Cl{\cdot}N{:}N{\cdot}SPh$, prepared from parachlorodiazonium chloride and phenylic hydrosulphide, crystallises from ether at 0° in yellow, rectangular plates melting at 60—62°; the yield is 84 per cent. of the theoretical. The ether, unlike the oxygen derivative, is only very slowly attacked by glacial acetic acid, and the product does not combine with $\beta$-naphthol; it is readily soluble in presence of sodium methoxide, but at low temperatures undergoes no further change. When heated with alcohol, nitrogen, parachlorophenylic sulphide, and phenylic bisulphide are formed. During the preparation of the ether, a highly unstable compound, possibly the "syn" derivative, is formed if the liquid is cooled so that a portion freezes; it evolves nitrogen below 0°, and on one occasion exploded at this temperature while still moist. *Parabromodiazobenzenethiophenyl ether*, $C_6H_4Br{\cdot}N{:}N{\cdot}SPh$, from parabromodiazonium chloride, crystallises in dark, reddish-brown plates, melts at 44°, and is less stable than the chloro-derivative; the yield is about 30 per cent. of the theoretical. *Pariododiazobenzenethiophenyl ether* is even less stable than the bromo-derivative, and is prepared in a similar manner. *Orthochlorodiazobenzenethiophenyl ether*, evolves no nitrogen during its preparation; like the preceding compound, it is oily. *Dichlorodiazobenzenethiophenyl ether*, $C_6H_3Cl_2{\cdot}N{:}N{\cdot}SPh$ [N : Cl : Cl = 1 : 2 : 4], crystallises in golden plates, and melts at 55—56°. The corresponding *dibromo-* and *diiodo*-derivatives and *tribromodiazobenzenethiophenyl* *ether*, $C_6H_2Br_3\cdot N{:}N\cdot SPh$ [$Br_3 = 2:4:6$], are difficult to purify, and apparently are liquid at 0°.

*Antiparanitrodiazobenzenethiophenyl ether*, $NO_2\cdot C_6H_4{:}N{:}N\cdot SPh$, crystallises from warm alcohol in golden plates, melts at 96—97°, and is the most stable compound of this class hitherto prepared; as the oxy-ether is similarly characterised, the nitro-group appears to be specially favourable to the production of compounds possessing the anti-configuration. Antinitrodiazobenzene hydroxide does not react with phenylic hydrosulphide, but the sodium salt (sodium nitrophenylnitrosamine) yields the diazo-thio-ether and sodium hydroxide when treated with phenylic hydrosulphide in alcoholic solution. Paranitrobenzenediazonium perbromide is formed by the action of bromine on the thio-ether; with iodine, paranitroiodobenzene is probably formed, whilst iodine chloride yields a compound which melts at 150—156°, and is possibly nitrochloriodobenzene.

*Syn-sodium diazosulphanilate thiophenyl ether*, $SO_3Na\cdot C_6H_4\cdot N{:}N\cdot SPh$, is readily prepared by the interaction of phenylic hydrosulphide and diazosulphanilic acid in alkaline solution at 0°, but unless alkali is present in considerable excess the reaction proceeds slowly; it crystallises in yellow plates, and, when dry, is stable at the ordinary temperature, and in aqueous solution at 0°; the yield is about 80 per cent. of the theoretical. The *silver salt* is dark brown, and, like the sodium salt, immediately decomposes into its constituents when acidified with hydrochloric acid. The "anti" sodium salt does not react with phenylic hydrosulphide. The diazophenols combine with phenylic hydrosulphide in neutral, alkaline, and acid solution, but the products were not investigated on account of their great instability. When the free diazophenols, prepared by the action of silver oxide on the hydrochlorides, are treated at 0° with hydrogen sulphide, compounds are formed which probably are additive products of hydrogen sulphide and diazophenol hydrosulphide, $OH\cdot C_6H_4\cdot N{:}N\cdot SH,H_2S$. The *para*-compound crystallises in deep red, microscopic needles, melts and decomposes at 74—75°, is unstable above 0°, and decomposes in contact with indifferent solvents, such as chloroform, light petroleum, and particularly ether, into sulphur, nitrogen, hydrogen sulphide, and probably phenol. The *ortho*-derivative resembles the preceding compound, melts at 69—70°, and may be purified by dissolving it in cold glacial acetic acid and precipitating with ice-cold water.

J. B. T.

**Thiodiazo-derivatives.** By EUGEN BAMBERGER and E. KRAUS (*Ber.*, 1896, **29**, 272—286; compare Hantzsch and Freese, preceding Abstr.).—*Diparanitrodiazobenzene sulphide*,



$$\mathrm{NO_2\cdot C_6H_4\underset{\underset{N}{\vdots}}{N}\cdot S\cdot \underset{\underset{N}{\vdots}}{N}C_6H_4NO_2,}$$

is prepared by the action of hydrogen sulphide at 0°, on aqueous paranitrodiazobenzene chloride solution which has been almost neutralised with soda; the product is treated with ammonia to remove any diazomercaptan hydrosulphide (see below); it crystallizes from acetone, on the addition of ice-cold water, in sulphur-yellow, lustrous needles, which explode at 89°, and also when pressed, or when treated with concentrated sulphuric acid or nitric acid vapour; and, on one occasion, when it was gently heated on the water bath while covered with a large amount of light petroleum. It is insoluble in alkali at the ordinary temperature, and when heated, decomposes; concentrated alcoholic potash decomposes it at the ordinary temperature; in acetone solution, it gives a violet-red coloration with soda, probably caused by the formation of a formazyl-derivative. Lead acetate added to the diazosulphide in alcoholic solution gives lead sulphide; it combines instantaneously with $\alpha$-naphthol when warmed more slowly at the ordinary temperature, giving an orange-yellow coloration changing to violet with alkali; with $\alpha$-naphthylamine the sulphide, in acetic acid solution, gives immediately a violet coloration, and it also combines directly with alkaline $\beta$-naphthol. With resorcinol, a characteristic violet-red coloration is produced. Benzene reacts at the ordinary temperature with the diazosulphide forming paranitrodiphenyl, paradinitrophenylic bisulphide, sulphur, and nitrogen; the reaction takes place in two stages, nitrodiphenyl, nitrogen, and hydrogen sulphide are first formed, and the latter converts a portion of the diazo-sulphide into dinitrophenylbisulphide. Toluene and pyridine react like benzene, paranitrophenyltolyl and paranitrophenylpyridine, respectively, being produced, together with dinitrophenylic bisulphide and sulphur.

*Paranitrodiazobenzene mercaptanhydrosulphide*,

$$NO_2\cdot C_6H_4\cdot N(SH)\cdot NH\cdot SH,$$

is prepared by the action of hydrogen sulphide at 0° on aqueous paranitrodiazobenzene chloride solution, in presence of hydrogen chloride in excess; it is purified by dissolving it in ammonia and continuously adding the solution to well cooled acetic acid, the precipitate is then crystallised from light petroleum, or from acetone by the addition of ice-cold water. It forms red, metallic, lustrous needles with a blue reflex, melts at 86°, is decomposed when heated with alcohol or acetone, readily dissolves in alkalis and ammonia, and is reprecipitated by acids. It does not combine with phenols in presence of either alkali or acid. The molecular weight was determined by the cryoscopic method; the yield is about 50 per cent. of the nitraniline employed. The *lead* salt is pale red, but becomes brown with a bronze lustre when dry; the *silver* salt is brownish-red and soon blackens; the *mercuric* salt, $Hg\left(N{<}\begin{matrix}N(C_6H_4\cdot NO_2)\\ S\text{———}Hg\end{matrix}{>}S\right)_2$, is pale orange-yellow and crystalline. When heated, the mercaptan hydrosulphide solidifies immediately after melting, the solid then consisting of paranitraniline, paranitrophenylhydrazine, dinitrophenylic bisulphide, and sulphur, whilst hydrogen sulphide, nitrogen, and, in small quantity, nitrobenzene are evolved. The same result is obtained by boiling the mercaptan hydrosulphide for a considerable time with light petroleum or alcohol. The first stage in this decomposition probably consists in a resolution of the mercaptan hydrosulphide into nitrodiazobenzene mercaptan and hydrogen sulphide, the latter then reduces a portion of the former to nitrophenylhydrazine, nitraniline, and sulphur, whilst the remainder of the mercaptan is oxidised by the air to nitrogen and dinitrophenylic bisulphide; the last compound is formed by the action of air on the mercaptan hydrosulphide in ammoniacal solution, and also by the action of iodine; it melts at 180·5°, and not at 168—173° as stated by Leuckart. Benzene and toluene react with the mercaptan hydrosulphide like alcohol, but in addition, nitrodiphenyl and nitrophenyltolyl respectively, are formed.

*Diparanitrodiazobenzene bisulphide*, $S_2(N{:}N{\cdot}C_6H_4{\cdot}NO_2)_2$, is prepared like the above mercaptan hydrosulphide, except that the treatment with hydrogen sulphide is prolonged, the hydrosulphide is removed from the product by treating it with ammonia, and the residue is extracted at 0° with acetone in which the bisulphide dissolves more readily than the monosulphide. It is purified in a similar manner to the latter, crystallises in lustrous, pale sulphur-yellow needles or plates, melts and decomposes at 120—123°, does not explode, and is stable at the ordinary temperature, but decomposes when heated with acetone, alcohol, or benzene. The bisulphide dissolves in alkali only when boiled, gas is evolved and the solution becomes reddish-brown; in alcoholic or acetone solution, it gives a claret coloration with alkali; with $\alpha$-naphthylamine, a violet-red coloration is slowly produced; with $\alpha$-naphthol and alkali, a dark brownish-red coloration is obtained which changes slowly to violet. With resorcinol, the mono- and bisulphides react almost identically, whilst with benzene, the bisulphide yields the same products as the monosulphide, but the action proceeds less readily. Isoparanitrodiazobenzene hydroxide, with hydrogen sulphide, yields, at −10°—0°, paranitraniline and paranitrophenylhydrazine. Dinitrodiazobenzene sulphide, in presence of sulphuric acid, is converted by the action of hydrogen sulphide into the bisulphide, and the mercaptan hydrosulphide; this confirms the authors' view that, with nitrodiazobenzene, the hydrogen sulphide first yields the monosulphide, a part of the latter being then converted into bisulphide, and part into the hydrosulphide. As yet the preceding formulæ can only be regarded as provisional.

J. B. T.

**Salts of Phenylhydrazine and of $\alpha$-Methylphenylhydrazine.** By Siro Grimaldi (*Real. Accad. Lincei*, 1893, i, 483—491).—*Phenylhydrazine hydriodide*, $NHPh{\cdot}NH_2,HI$, crystallises in white scales or needles melting at 120—122°, and is readily soluble in water, alcohol, or acetone, giving neutral solutions; its solubility in water is increased by the addition of alkali iodides. With potassium iodide and magnesium iodide, it yields double *salts* of the compositions $C_6H_8N_2,HI,KI$, and $(C_6H_8N_2,HI)_2,MgI_2$. The *hydrofluoride*,

$$NHPh{\cdot}NH_2,HF,$$

crystallises in lustrous, white laminæ, and is soluble in water or alcohol; its solubility in water is increased by adding alkali fluorides and its aqueous solution is neutral to test papers. It can be easily sublimed unchanged, and forms double *salts* of the compositions $C_6H_8N_2,HF,KF$; $C_6H_8N_2,HF,NaF$; $C_6H_8N_2,HF,LiF$, and

$$(C_6H_8N_2,HF)_2,MgF_2,$$

which crystallise in white laminæ and are very soluble in water.

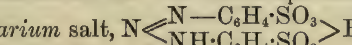
*α-Methylphenylhydrazine hydrofluoride*, $NMePh\cdot NH_2,HF$, crystallises in colourless laminæ, and is very soluble in water.

W. J. P.

**Constitution of Dicyanophenylhydrazine and Bladin's Triazole Compounds.** By AMERICO ANDREOCCI (*Real. Accad. Lincei*, 1893, ii, 302—310).—The author replies to Bamberger and de Gruyter's criticisms (Abstr., 1894, i, 23) of his previous work (Abstr., 1892, 636).

W. J. P.

**Migration of the Diazo-Group.** By C. SCHRAUBE and M. FRITSCH (*Ber.*, 1896, **29**, 287—294).—Diazosulphanilic acid and paratoluidine hydrochloride at 0° yield sulphanilic acid and diazoparatoluene chloride, as Griess has previously shown; the course of the reaction may be followed by means of alkaline β-naphthol solution, with which the diazotoluene forms an insoluble compound; it is complete after 24 hours, but the presence of hydrochloric acid in large excess completely prevents the change. In neutral solution, the above compounds immediately yield the diazoamido-derivative, $C_6H_4Me\cdot N\colon N\cdot NH\cdot C_6H_4\cdot SO_3H$, in the form of a yellow *toluidine* salt; the *sodium* salt crystallises in long, thin, pale-yellow plates; the *disodium* salt is deep yellow; the *calcium* salt is pale yellow, and crystalline; the *barium* salt is sparingly soluble. When treated with acids, the sodium salt yields sulphanilic acid and diazotoluene chloride. In alkaline solution, diazosulphanilic acid and paratoluidine yield a diazoamido-derivative of sulphanilic acid and diazoamidotoluene, the *barium* salt,



$N{<}\begin{matrix}N—C_6H_4\cdot SO_3\\NH\cdot C_6H_4\cdot SO_3\end{matrix}{>}Ba$,

of the former, being crystalline. With less alkali, the mixed diazoamido-compound (see above) is also formed. Diazotoluene chloride and sulphanilic acid are without action in presence of mineral acids, but, with sodium sulphanilate, the reaction is normal, whilst the two sodium salts yield the two diazoamido-compounds. Paranitrodiazobenzene chloride and paratoluidine readily yield a diazoamido-derivative in acid solution, but in presence of a large excess of acid, the diazo-group migrates and the reaction may be readily followed by testing portions of the liquid with α-naphthylamine hydrochloride in hydrochloric acid solution. In neutral or faintly acid solution, the diazoamido-derivative is formed, and is quickly resolved by hydrochloric acid into paradiazotoluene and paranitraniline. The migration of the diazo-group resembles the formation of diazoamido-derivatives, as in both cases the imido-group combines with the most negative radicle, and the diazo-group with the positive one. Following V. Meyer, the interaction of diazosulphanilic acid and paratoluidine in alkaline solution is regarded as taking place in several stages, an additive compound, $C_6H_4Me\cdot NH\cdot N(OH)\cdot NH\cdot C_6H_4\cdot SO_3H$, being first formed, which combines with a second molecule of diazosulphanilic acid forming a compound $C_6H_4Me\cdot NH\cdot N(OH)\cdot N(C_6H_4\cdot SO_3H)\cdot N(OH)\cdot NH\cdot C_6H_4\cdot SO_3H$, corresponding with von Pechmann's bisdiazobenzene anilide; and, finally, this is resolved into diazoamidosulphanilic acid and diazotoluene which, with the remaining toluidine, yields diazo-amidotoluene. The results obtained with diazotoluene and sulphanilic acid in alkaline solution are explained in a similar manner. J. B. T.

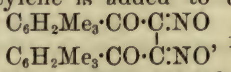
**Action of Nitrosobenzene on Amido-compounds.** By Eugen Bamberger (*Ber.*, 1896, **29**, 102—104; compare Mills, Trans., 1895, 925).—The author has studied the behaviour of numerous amido-compounds towards nitrosobenzene, bases of both the aromatic and the aliphatic series having been included in the investigation, the results of which will be shortly published.

According to Mills (*loc. cit.*), phenylhydrazine gives rise to azobenzene when treated with nitrosobenzene, Walther having obtained aniline; the author, however, has observed the production of *diazohydroxyamidobenzene*, $PhN:N\cdot N(OH)Ph$, crystallising in pale yellow, silky needles, which melt at 126—127°. This substance is also obtained from diazobenzene and phenylhydroxylamine, which are formed when the compound is treated with acids. Analogous diazohydroxyamido-compounds have been obtained from β-benzylhydroxylamine and β-methylhydroxylamine, namely, *diazobenzenehydroxyamidobenzyl*, $PhN:N\cdot N(OH)\cdot CH_2Ph$, which melts at 105°, and *paranitrodiazobenzenehydroxyamidomethane*, $NO_2\cdot C_6H_4\cdot N:N\cdot N(OH)Me$, which crystallises in silky, golden-yellow needles, and melts at 228°.

M. O. F.

**Influence of Methyl Groups in the Ortho-position in hindering the Formation of Oximes.** By Fritz Baum (*Ber.*, 1895, **28**, 3207—3212).—Hantzsch (Abstr., 1891, 36) has shown that both ketones and aldehydes, in which substitution has taken place in the two ortho-positions with respect to the carbonyl group, do not yield oximes. Feith and Davies (Abstr., 1892, 314) have also shown that acetylmesitylene yields no oxime, but at higher temperatures reacts with hydroxylamine hydrochloride, according to Beckmann's reaction, yielding acetomesidide. The author has investigated the action of hydroxylamine hydrochloride on dibenzoylmesitylene, mono- and di-acetylisodurene, acetylpentamethylbenzene, and mesitylglyoxylic acid, and finds that no oxime is formed in any case; mesitylglyoxylic acid, however, gave cyanomesitylene (m. p. 53°). Ethylic mesitylglyoxylate yields a compound which may be an oxime, and which is being subjected to further investigation.

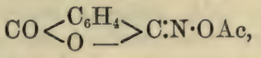
Acetylmesitylene, mono- and di-benzoylmesitylene, and propionylmesitylene, when treated with phenylhydrazine, yield no hydrazones. When acetylmesitylene is added to concentrated nitric acid, *dimesityldinitrosacyl*,



$$\begin{array}{l}C_6H_2Me_3\cdot CO\cdot C:NO \\ \qquad\qquad\quad\;\; | \\ C_6H_2Me_3\cdot CO\cdot C:NO\end{array},$$

is obtained; it crystallises in large, yellowish needles, melts at 141°, and, when boiled with alcoholic soda, yields mesitylcarboxylic acid. J. J. S.

**Action of Hydroxylamine on Methylic Phthalate.** By Giorgio Errera (*Gazzetta*, 1895, ii, 21—25).—Hydroxylamine acts on methylic phthalate under various conditions, yielding phthalylhydroxylamine, from which *phthalylacetoxylamine*,



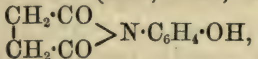
$$CO<{}^{C_6H_4}_{O\,—}>C:N\cdot OAc,$$

is readily prepared; this crystallises in monoclinic plates melting at 181°, and is sparingly soluble in alcohol or water; $a : b : c = 1{\cdot}97784 : 1 : 1{\cdot}11035$; $\beta = 85° 48'$. It is hydrolysed by boiling with water, yielding acetic acid and phthalylhydroxylamine; the latter gives a crystalline *ammonio*-derivative, which is very soluble in water, and readily loses ammonia in the air, giving phthalylhydroxylamine.

W. J. P.

**γ-Carbodiphenylimide.** By CARL SCHALL (*Ber.*, 1896, **29**, 270—271).—Von Miller and Plöchl have suggested (Abstr., 1895, i, 415) that γ-carbodiphenylimide is a mixture of the liquid α-, and the crystalline, β-compounds; in opposition to this view, the following facts are advanced. (1) With light petroleum, the surface of the γ-compound becomes granular, and is slowly converted into the β-form; the change corresponds exactly with that which takes place when vitreous arsenious anhydride passes into the crystalline modification, and is also slowly produced by gentle heating, during which no α-imide is volatilised. (2) Miller and Plöchl have shown that a concentrated benzene solution of the β-imide, at about the freezing point of benzene, contains, at the most, only traces of the α-compound; such a solution, after concentration under certain conditions, yields only the amorphous γ-compound. (3) When intimately mixed, the α- and β-compounds give a white, opaque mass, which is only viscid if it contains 4 parts of the α-imide. The γ-modification occasionally changes slowly and spontaneously into crystals consisting of needles and plates; it can scarcely be a solid solution, as such should, from analogy, be crystalline and not amorphous.

J. B. T.

**Action of Succinic acid on Paramidophenol and its Ethers.** By ARNALDO PIUTTI (*Ber.*, 1896, **29**, 84—86).—*Parahydroxyphenylsuccinimide*,  $\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}>N\cdot C_6H_4\cdot OH$, is obtained by fusing succinic acid with paramidophenol in molecular proportion; it crystallises in lustrous, colourless prisms, and melts at 275—276°. Hot potash converts it into *parahydroxyphenylsuccinamic acid*, which dissolves in water, alcohol, and acetic acid, and melts at 171—172°; the *barium* and *alkali* salts are readily soluble in water, the *lead* and *silver* salts are crystalline, and the *copper* salt is insoluble in water.

*Paramethoxyphenylsuccinimide* is produced on heating paranisidine hydrochloride or methacetin with succinic acid at 190°, and crystallises in colourless, prismatic needles, which melt at 162—163°; hydrolysis gives rise to *paramethoxyphenylsuccinamic acid*, which crystallises from water, and melts at 156—157°.

*Parethoxyphenylsuccinimide* (*pyrantine*) is obtained by fusing succinic acid with phenacetin, or with paraphenetidine hydrochloride; it crystallises in colourless, prismatic needles, and melts at 155°. Succinic acid and phenetidine are formed when the substance is treated with hot hydrochloric acid, and fusion with potassium hydrogen sulphate brings about the same result; coloration is developed by nitric acid, chromic acid, chlorine water, and ammonia, whilst fusion with potash, and treatment of the aqueous extract with a solution of calcium hypochlorite, yields a red liquid. *Parethoxyphenylsuccinamic acid* is obtained by hydrolysing the foregoing derivative; it crystallises from hot water in nacreous leaflets, and melts at 160—161°. The *sodium* salt is the soluble form of pyrantine, and possesses valuable physiological properties which recommend its application as a febrifuge. M. O. F.

**Action of Phenylic Isocyanate on Amido-acids.** By Carl Paal and Fritz Ganser (*Ber.*, 1895, **28**, 3227—3234; compare Abstr., 1894, i, 332).—In continuation of their work on amido-acids, the authors have studied the action of phenylic isocyanate on the alkali salts of the three amidocinnamic acids, of sulphanilic acid, and sarcosine.

*Orthophenylureidocinnamic acid*,

$$NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot CH{:}CH\cdot COOH,$$

crystallises in very small, felted needles, melts at 236°, is insoluble in water, only sparingly soluble in chloroform, carbon bisulphide, and ether, but readily in hot alcohol and acetic acid. The *alkali* salts are not soluble in concentrated, alkaline liquids; the *silver* salt forms an amorphous mass, which is practically insoluble in water, and is extremely sensitive to light. The *ethylic* salt crystallises in needles, melts at 112°, and is readily soluble in most organic solvents. When the acid is reduced with sodium amalgam and water, it yields *orthophenylureidophenylpropionic acid*, which melts at 168°, and is readily soluble in hot alcohol, acetone, and ethylic acetate. The *dibromide*, $NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot CHBr\cdot CHBr\cdot COOH$, melts at 227°, and is readily soluble in alcohol and ethylic acetate, but only sparingly in most other organic solvents.

*Metaphenylureidocinnamic acid* melts at 249°, and is more sparingly soluble in most solvents than the ortho-acid. The *ethylic* salt crystallises in needles, melts at 198°, and is readily soluble in chloroform and ethylic acetate. The *ammonium*, *sodium*, and *silver* salts resemble those of the ortho-acid. The *dibromide* crystallises in small plates, and melts at 240°. *Metaphenylureidophenylpropionic acid* melts at 180°.

*Paraphenylureidocinnamic acid* crystallises in brilliant glistening needles, and melts at 252°; the *ethylic* salt melts at 204°, and the dibromide begins to decompose at 165°. *Paraphenylureidophenylpropionic acid* melts at 218°, and is practically insoluble in ether.

*Paraphenylureidobenzenesulphonic acid*, $NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot SO_3H$, obtained from sodium sulphanilate and phenylic isocyanate, crystallises in colourless needles or prisms, and begins to decompose at 270°, but is not completely melted at 300°. It is practically insoluble in ether, chloroform, and benzene, but readily in ethylic alcohol, acetone, and acetic acid. The *calcium* salt crystallises from its hot aqueous solution in glistening, rhombic plates, which contain $3\frac{1}{2}H_2O$.

The *barium* salt is anhydrous, and is only sparingly soluble in hot water. The *silver* salt crystallises from hot water in large prisms, and is not decolorised by exposure to light. The *ethylic* salt crystallises in colourless needles, melts at 155°, and is readily soluble in ether, alcohol, acetone, &c.

*ab-Methylphenylureidoacetic acid*, $NHPh{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}COOH$, crystallises in needles, melts at 102°, and is insoluble in ether and chloroform, but readily dissolves in sodium hydroxide, boiling water, ethylic acetate, and water. The silver salt could not be obtained; the *ethylic* salt crystallises in small needles, and melts at 75°.

J. J. S.

**Derivatives of Metadibromoparahydroxybenzaldehyde.** By CARL PAAL and G. KROMSCHRÖDER (*Ber.*, 1895, **28**, 3234—3236; compare this vol., i, 40).—The dibromohydroxybenzaldehyde [$Br_2 : OH = 3 : 5 : 4$], previously described, readily combines with aniline to form *dibromoparahydroxybenzylideneaniline*, $OH{\cdot}C_6H_2Br_2{\cdot}CH{:}NPh$. It is readily soluble in warm alcohol and in most organic solvents, crystallises in compact, red crystals, or from alcohol in small, metallic, violet coloured plates containing alcohol of crystallisation. It melts at 147°.

*Metadibromoparahydroxybenzylideneparatoluidine* crystallises from its alcoholic solution in plates, which are characterised by a blue, metallic lustre, and melts at 157°.

*Metadibromoparahydroxybenzylidene-α-naphthylamine* crystallises in yellowish needles, melts at 146°, and does not combine with alcohol.

*Metadibromoparahydroxybenzaldoxime* crystallises in short, white needles, melts at 194°, and is readily soluble in alcohol, ether, and ethylic acetate.

*Metadibromoparahydroxybenzoic acid*, obtained by the oxidation of the aldehyde with potassium permanganate (1 per cent. solution), crystallises in colourless needles and melts at 268°. J. J. S.

**Isomerism of Trithioaldehydes.** By EMIL WÖRNER (*Ber.*, 1896, **29**, 139—160).—Baumann and Fromm (Abstr., 1889, 852; 1890, 25 and 26; 1891, 1008 and 1050) have shown that benzaldehyde, anisaldehyde, methyl- and isobutylsalicyl-aldehyde, cinnamaldehyde, and furfuraldehyde each yield two stereoisomeric trithioaldehydes, a lower melting, or α-, form, and a higher melting, or β-, form. Kopp (Abstr., 1894, i, 128) found that the three hydroxybenzaldehydes yield, each, one trithio-derivative, which he termed the β-modification, as it was not changed by the action of iodine. The author has repeated some of Kopp's experiments, and has arrived at similar results. Thus, with parahydroxybenzaldehyde under the most varying conditions, only a single trithio-compound could be obtained; it crystallises with 2 mols. of benzene (Kopp states 3 mols.), which it partially loses on exposure to the air, and melts at 215°.

*Parabenzyloxybenzaldehyde*, obtained by shaking the hydroxyaldehyde in strong alkaline solution with the requisite quantity of benzylic chloride, crystallises in short needles, melts at 72°, and is readily soluble in alcohol, chloroform, benzene, and ether. If hydrogen sulphide is passed into an alcoholic solution to which alcoholic hydrogen chloride has been added, *α-trithioparabenzyloxybenzaldehyde* is obtained; it crystallises in colourless needles, melts at 127°, and is sparingly soluble in alcohol and ether, but readily in chloroform, benzene, and acetone. When treated with iodine, it passes into the *β-modification*, which also crystallises in colourless needles, melts at 198—199°, contains 2 mols. of benzene of crystallisation, and is more sparingly soluble in all solvents than the α-compound. By using $\frac{1}{4}$ vol. of alcoholic hydrogen chloride to 1 vol. of a 5 per cent. solution of the benzylbenzaldehyde, about equal quantities of the α- and β-modifications are obtained.

Vanillin yields only one *trithiovanillin*, which melts at 235—237°, and is only sparingly soluble in alcohol, benzene, and ether, more readily in chloroform and acetone; when the crystals are boiled with benzene, they take up 2 mols. of benzene of crystallisation. *Trithiobenzoylvanillin*, obtained by the action of benzoic chloride on trithiovanillin, crystallises in colourless needles, begins to sinter at 155°, and melts at 164°. *Benzoylvanillin* melts at 75°, and is readily soluble in alcohol, chloroform, and ether.

Methylvanillin yields two isomeric trithio-derivatives, which may be separated by means of benzene. *α-Trithiomethylvanillin* crystallises in small needles, melts at 168°, and is extremely readily soluble in benzene, but only sparingly so in alcohol; when treated, in benzene solution, with iodine, it is transformed into the *β-compound*, which crystallises with 2 mols. of benzene or thiophen, and melts at 220°.

*α-Trithiopiperonal* crystallises in small, colourless needles, melts at 183°, is sparingly soluble in alcohol or ether, and readily in chloroform, acetone, and benzene. *β-Trithiopiperonal* melts at 236°, and is more sparingly soluble than the α-compound.

*Trithiogentisic aldehyde* apparently exists in one form only; this crystallises in small, white needles, melts and decomposes at 190°, and is very readily soluble in alcohol.

*α-Trithiodimethylgentisic aldehyde* is a colourless, crystalline powder, melts at 95—96°, and is readily soluble in benzene, acetone, and chloroform. The *β-compound* crystallises with 2 mols. of benzene and melts at 180°. It is practically insoluble in alcohol, and only sparingly soluble in chloroform.

*α-Trithiocumaldehyde* crystallises in long, white needles, and melts at 165°; the *β-compound* could not be obtained directly, but only by the action of iodine on the α-isomeride; it crystallises with 3 mols. of benzene, and melts at 205°.

*α-Trithiometatolualdehyde* crystallises in white needles and melts at 144°; the *β-isomeride* crystallises in white, glistening needles, which contain 3 mols. of benzene, and melts at 225°.

*α-Trithioparatolualdehyde* melts at 149—150°, and the *β-compound* at 180°; the latter crystallises with 3 mols. of benzene.

*α-Trithio-orthobromobenzaldehyde* melts at 75°, is only sparingly soluble in alcohol, but readily in ether, benzene, chloroform, and acetone; the *β-isomeride* melts at 155°, and crystallises with 1 mol. of benzene.

*α-Trithioparabromobenzaldehyde* is readily soluble in benzene, and crystallises in small needles, which melt at 174°. The *β-compound* crystallises with 1 mol. of benzene, melts at 203°, and is more sparingly soluble than the α-isomeride.

Metanitrobenzaldehyde yields a trithio-derivative, which melts at 180—190°; it was found impossible to purify the compound, as it is insoluble in all organic solvents. Orthonitrobenzaldehyde gave a similar result.

Metanitrocumaldehyde gave only one *trithio-derivative*, which melts at 118°, and is not acted on by iodine. Metanitroanisaldehyde melts at 72°, whereas Einhorn and Grabfield (Abstr., 1888, 478) give 83·5° as the melting point. A *dinitroanisaldehyde*, melting at 86°, was also obtained. *Trithiometanitroanisaldehyde* is a yellowish, crystalline powder, and melts at 108°; the *trithiodinitroaldehyde* melts at 188°, is readily soluble in benzene, chloroform, and acetone, but only sparingly in alcohol or ether.

The author summarises his results as follows.

1. Substituted aromatic aldehydes yield two stereoisomeric trithio-derivatives only when the substituting groups are of a positive or indifferent nature. Aldehydes with negative substituting groups yield one trithio-aldehyde, namely, the β-modification. If the negative character of the hydroxyl group of a phenolic aldehyde is changed by methylation, &c., then the resulting compound yields two isomeric trithio-derivatives.

2. All α-trithioaldehydes may be converted into the β-modifications by means of iodine.

3. The trithioaldehydes are most easily obtained from phenolic aldehydes or aldehydes containing negative groups; if positive groups are present, polymerides of high molecular weight are apt to be formed.

J. J. S.

**Metadihydroxyphenyl Ketones.** By ADOLPH CLAUS and M. HUTH (*J. pr. Chem.*, 1896, [2], **53**, 39—42).—By acetylating the alkylic ethers of resorcinol (by treating them with acetic chloride and aluminium chloride in carbon bisulphide), it is possible to obtain, according to the conditions of the experiment, the dialkyloxyacetophenone, the alkyloxyhydroxyacetophenone, or dihydroxyacetophenone itself. The compound last mentioned melts at 178°, and is therefore not identical with that (m. p. 142°) obtained by Nencki and Sieber (Abstr., 1881, 591) from resorcinol by acting on it with glacial acetic acid and zinc chloride. This lack of identity extends to the derivatives of the two compounds, as will be seen from the following list of melting points.

| | Nencki and Sieber. | Claus and Huth. |
|---|---|---|
| Dihydroxyacetophenone...... | 142° | 178° |
| Oxime therefrom | 202° (decomposes) | 223—225° (decomposes). |
| Monethyl ether.. | 48° | 108° |
| Diethyl ether... | 68—69° | 152° |
| Oxime therefrom | 122° | 240° (decomposes). |

The authors note a curious interchange between these two compounds and their derivatives, which seems to betoken an alteration of orientation, brought about by the influence of the alkyl groups. The identity of composition and molecular weight of the two dihydroxyacetophenones has been established. A. G. B.

**Introduction of two Acetyl Groups into Aromatic Hydrocarbons.** By FRITZ BAUM and VICTOR MEYER (*Ber.*, 1895, **28**, 3212—3215).—Hitherto it has been found impossible to introduce two acetyl groups into aromatic hydrocarbons by the Friedel-Crafts method, but the authors show that a diacetyl derivative of durene may be obtained if the action is carried on without prolonged heating, and in the presence of an excess of acetic chloride; if, however, the mixture is heated for some time, as in the usual Friedel-Crafts synthesis, the monacetyl derivative alone is obtained. Benzene and mesitylene apparently do not yield diacetyl derivatives under similar conditions.

*Diacetyldurene* melts at 178°, distils between 323 and 326°, and crystallises from ether in glistening, six-sided plates.

*Diacetylisodurene* melts at 121° and distils at 312—317°.

*Acetylisodurene* is an oil, and boils at 255—260°.

*Dipropionyldurene* melts at 176° and boils at 330—335°.

*Propionyldurene* melts at 79° and distils at 265—270°.

The authors have not yet proved that the second acetyl group does not replace one of the methyl groups of durene. J. J. S.

**Formation and Hydrolysis of Ethereal Salts.** By VICTOR MEYER (*Ber.*, 1895, **28**, 3197—3201; compare Abstr., 1894, i, 243, 463; 1895, i, 93, 228, 466).—The author now shows that phenylacetic acid is much more readily etherified than benzoic acid. Thus, a solution of phenylacetic acid in methylic alcohol, containing only 3 per cent. of hydrochloric acid, yields 50 per cent. of ethereal salt after five minutes; benzoic acid under the same conditions yields no trace of ethereal salt. This points to the fact that the two methylene hydrogen atoms in phenylacetic acid exert no restraining influence on the formation of ethereal salts, whereas the two methin hydrogen atoms in benzoic acid do.

The relationship between the formation of ethereal salts and the hydrolysis of the corresponding nitriles is not so simple as it is generally considered. For instance, triphenylacetic acid is etherified with difficulty and triphenylacrylic acid readily, but the nitrile of the former acid is much more easy to hydrolyse than that of the latter.

It has been previously shown that mesitylformic (mesitylenecarboxylic) acid, when treated for 12 hours in the cold, yields no ethereal salt, whereas, at the boiling point of the alcohol, a considerable amount of ethereal salt is formed. It is now shown that, if hydrogen chloride is kept passing through a solution of this acid in methylic alcohol (at 0°) during a week, no less than 26 per cent. is converted into the ethereal salt, and, at the end of two weeks, 46 per cent. Symmetrical trinitrobenzoic acid, when treated in the same way for a week, gave only 0·7 per cent. of ethereal salt. The mono-substituted derivatives of benzoic acid, in which the substituting groups were $CH_3$, Cl, Br, I, and $NO_2$, have been investigated, and, in each case, the ortho-acid was the one which took longest to etherify, and the corresponding ethereal salt the one most difficult to hydrolyse.

Other alcohols besides methylic alcohol have been tried, and yield similar results. J. J. S.

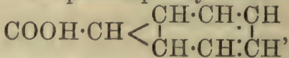
**A New Phenomenon in the Formation of Ethereal Salts by the action of Alcohol and Hydrogen Chloride on Aromatic Acids.** By A. Shukoff (*Ber.*, 1895, **28**, 3201—3202).—The author has studied the action of methylic alcohol and hydrogen chloride on benzoic and phenylacetic acids; he finds that a given concentration of the hydrogen chloride gives the maximum of ethereal salt in a given time, and that a stronger or weaker alcoholic solution of the hydrogen chloride yields smaller quantities of ethereal salt. Thus at 0° phenylacetic acid gives a maximum of methylic salt when treated with a solution containing 40 grams of hydrogen chloride to 100 of methylic alcohol; at 22°, benzoic acid gives a maximum of ethereal salt with 50 parts of hydrogen chloride to 100 of alcohol.

Heinrich Goldschmidt suggests that the more concentrated solutions of hydrogen chloride in alcohol readily form the alkylic chloride and water, and that it is the water thus formed which has a retarding influence on the formation of ethereal salts. J. J. S.

**Etherification by means of Alcoholic Hydrogen Chloride.** By Heinrich Goldschmidt (*Ber.*, 1895, **28**, 3218—3227).—The author has made experiments on the velocity of etherification of benzoic acid, by means of alcohol, in the presence of varying quantities of hydrogen chloride; the results show that the velocity of etherification in the case of dilute solutions of hydrogen chloride is proportional to the concentration of the hydrogen chloride, but the addition of even small quantities of water retards the velocity to a considerable extent. Hydrogen bromide has very much the same influence on the velocity of etherification as hydrogen chloride, but picric acid has far less influence. Substituted benzoic acids are etherified at different rates by alcoholic hydrogen chloride; in all cases, the ortho-substituted acids are much more slowly etherified (V. Meyer, this vol., i, 228). As a rule, substitution in the meta-position increases the velocity, except in the case of the nitro-group, and para- are more slowly etherified than meta-compounds. The author also confirms V. Meyer's statement that phenylacetic acid is more easily etherified than benzoic acid. J. J. S.

**Formation of Ethereal Salts from Acids and Alcohols.** By Rudolf Wegscheider (*Ber.*, 1895, **28**, 3127—3128; compare Abstr., 1895, i, 499).—The action of methylic alcohol on hemipinic acid, in presence of an eighth part of its volume of concentrated sulphuric acid gives rise to the β-monomethylic salt; etherification by means of sulphuric acid has, therefore, the same result as when hydrogen chloride is employed, and the author in consequence holds the view that in the former case also etherification depends on the intermediate production of an additive compound. When equal volumes of methylic alcohol and sulphuric acid are used, the normal salt of hemipinic acid is formed; symmetrical tribromobenzoic acid is also partially etherified when thus treated, although, under the conditions first described, the last-named acid yields no ethereal salt. There is no appreciable formation of ethereal salt when a mixture of methylic alcohol and sulphuric acid acts on hydrogen potassium hemipinate during a short period.

When hemipinic acid is heated with methylic alcohol at 100°, $\alpha$-monomethylic hemipinate is produced, probably owing to the intermediate formation of the anhydride, as this substance is obtained in small quantity when hemipinic acid is heated at 100°, benzoic acid, moreover, yields no ethereal salt under these conditions. The formation of the $\alpha$-modification in the absence of sulphuric acid or hydrogen chloride clearly indicates that the effect produced by these agents is not due to dehydrating action. M. O. F.

**Pseudophenylacetic acid.** By EDUARD BUCHNER (*Ber.*, 1896, **29**, 106—109).—The author proposes to apply the names pseudophenylacetic acid, pseudotolylacetic acid, &c., to the acids which are obtained by the action of ethylic diazoacetate on the aromatic hydrocarbons, and are isomeric with phenylacetic acid, &c. *Sodium pseudophenylacetate* is obtained as a crystalline powder by the action of sodium ethoxide on the ethylic salt. It cannot be recrystallised, gradually increases in weight when preserved in dry air, and is at once oxidised by potassium permanganate. Like the ethylic salt and the amide, it forms a cherry-red solution in concentrated sulphuric acid, the colour gradually changing to indigo-blue. *Pseudophenylacetamide* crystallises from water in large, vitreous tablets, which melt at 141°. When hydrolysed by aqueous soda, it yields an unsaturated acid, which melts at about 71°, and does not give the characteristic reaction of the amide with sulphuric acid. *Sodium pseudotolylacetate* closely resembles the corresponding salt of pseudophenylacetic acid. Pseudotolylacetic acid unites with four atoms of bromine to form an unstable *tetrabromide*, which loses hydrogen bromide when kept, a solid substance being left, which has the formula $C_9H_9Br_3O_2$. This compound cannot be recrystallised, but may be reprecipitated from its solution in alkalis; it melts at 80—85°. The corresponding *derivative* of pseudophenylacetic acid melts at 84—86°. When pseudotolylacetic acid is passed through a red-hot tube, about 10 per cent. of paraxylene is formed. Pseudophenylacetic acid yields about 7 per cent. of terephthalic acid when oxidised with nitric acid, whilst this acid is accompanied by benzoic acid when alkaline potassium permanganate is used. The constitution of pseudophenylacetic acid is best represented by the formula  $COOH\cdot CH<\begin{matrix} CH\cdot CH\cdot CH \\ | \qquad\quad | \\ CH\cdot CH{:}CH \end{matrix}$, which admits of a simpler explanation of the reactions of the acid than that proposed by V. Meyer (*Ber.*, 1890, **23**, 617), in which the COOH·CH group is attached at the para- instead of the ortho-positions.

A. H.

**Tetramethylbenzoic acids.** By ADOLPH CLAUS (*J. pr. Chem.*, 1895, [2], **52**, 529—532).—In reference to V. Meyer's recent publication (this vol., i, 170), the author draws attention to the work which has been done by himself and his pupils on the oxidation of the methyl duryl ketones (Abstr., 1888, 275; 1889, 50). Attempts to purify the tetramethylbenzoic acids then described have succeeded to some extent, and it is shown that the 2 : 3 : 5 : 6-acid melts at 127°, not 109° (*loc. cit.*).

The oxidation of symmetrical tetramethylbenzoic acid by permanganate yields, under all conditions, dimethylbenzenetricarboxylic acid, whilst similar treatment of asymmetrical tetramethylbenzoic acid yields a dicarboxylic acid, in which the new carboxyl group is in the para-position, for by distillation with soda-lime it gives pseudocumene. Details of this research will follow shortly.

Contrary to Victor Meyer's rule, all three acids are equally easily etherified by hydrogen chloride in methylic and ethylic alcohol. The methylic and ethylic salts of symmetrical tetramethylbenzoic acid are crystalline, the former melting at 79—81°, and the latter at 47—48°. The methylic and ethylic salts of the other acids are viscid oils.

Some criticisms of V. Meyer's paper are given. A. G. B.

**Action of Ammonia on Ethylic Benzoylacetate.** By CARL GOLDSCHMIDT (*Ber.*, 1896, **29**, 105).—Ammonia unites with ethylic benzoylacetate to form an *additive product*, $COPh\cdot CH_2\cdot COOEt,NH_3$, which crystallises from alcohol in plates, having a satiny lustre, and melting at 178°. It sublimes when heated, and yields ammonia when treated with aqueous soda. Methylamine converts ethylic benzoylacetate into a white compound which gradually loses water and changes into *ethylic β-methylimidophenylpropionate*, $NMe{:}CPh\cdot CH_2\cdot COOEt$. A. H.

**Regularity in the Decomposition of Aromatic Ketonic Acids.** By FELIX MUHR (*Ber.*, 1895, **28**, 3215—3218).—Victor Meyer has previously shown (Abstr., 1895, i, 467) that symmetrical trimethyl-β-benzoylpropionic acid is decomposed by hydriodic acid into mesitylene and succinic acid. The author shows that the same decomposition may be brought about by heating the acid for five hours at 150° with hydrochloric acid.

*Paramethylbenzoylpropionic acid*, obtained by the action of a solution of toluene in carbon bisulphide on succinic anhydride in the presence of aluminium chloride, melts at 117°, and is not decomposed when heated with hydrochloric acid at 150°. Benzoylpropionic acid also is not acted on.

*Metadimethylbenzoylpropionic acid* (obtained from metaxylene), crystallises in colourless needles, melts at 106°, and is completely decomposed into metaxylene and succinic acid when heated with hydrochloric acid.

*Orthodimethylbenzoylpropionic acid* melts at 105°, and is not decomposed under the usual treatment.

Paradimethylbenzoylpropionic acid melts at 62°, whereas Claus gives 84° as the melting point, and is partially decomposed when heated at 150° with hydrochloric acid.

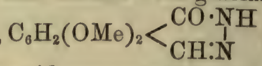
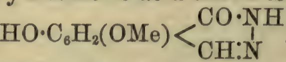
*Asymmetrical trimethylbenzoylpropionic acid* (from pseudocumene) melts at 98°, and is also partially decomposed when heated with hydrochloric acid.

*Symmetrical tetramethylbenzoylpropionic acid* (from durene) melts at 117°, and is decomposed in a similar manner, *pentamethylbenzoylpropionic acid* (white plates melting at 104°), is also decomposed, whereas *ethylbenzoylpropionic acid*, which crystallises in slender, lustrous needles, and melts at 90°, yields only traces of its decomposition products.

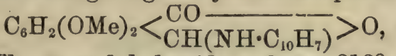
*Orthomethylethylbenzoylpropionic acid*, which forms very long, slender, lustrous needles melting at 78°, and *isopropylbenzoylpropionic acid*, crystallising in needles melting at 72°, are both practically unacted on when heated with hydrochloric acid at 150°, and about 50 per cent. of *paramethylisopropylbenzoylpropionic acid* (colourless plates melting at 70°) is decomposed, after heating for nine hours at 200° with hydrochloric acid.

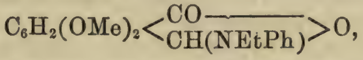
From these results it follows that only those acids are decomposed in which the side chain containing the carboxylic group is in the ortho-position relatively to one or both of the alkyl groups. J. J. S.

**Preparation of Ethylic Benzylideneacetoacetate.** By Emil Knoevenagel (*Ber.*, 1896, **29**, 172—174).—Ethylic acetoacetate and benzaldehyde in molecular proportion are mixed, cooled at −5°, piperidine (1 gram), diluted with two parts of alcohol, is added, and the liquid allowed to remain at the same temperature during 12—24 hours; the crystals are then separated and purified. The yield is 95 per cent. of the theoretical, and 100 grams of ethylic acetoacetate can be conveniently employed at once. The action probably takes place in two stages, benzylidenedipiperidine, $CHPh(C_5NH_{10})_2$, is first formed, and reacts with the ethylic acetoacetate, piperidine being regenerated. Diethylamine acts like piperidine. At the ordinary temperature, ethylic benzylidenediacetoacetate alone is formed from ethylic acetoacetate and benzaldehyde. J. B. T.

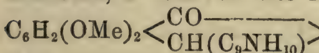
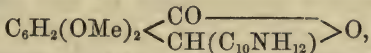
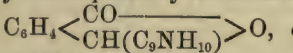
**Tautomerism of the Orthaldehydic Acids.** By Carl Liebermann (*Ber.*, 1896, **29**, 174—183).—*Opianic acid semicarbazone*, $COOH\cdot C_6H_2(OMe)_2\cdot CH:N\cdot NH\cdot CO\cdot NH_2$, is readily prepared by the action of opianic acid, in glacial acetic acid solution, on semicarbazide in aqueous solution; on the addition of water to the glacial acetic acid solution, it crystallises out in lustrous needles, melting at 187°. It quickly dissolves at the ordinary temperature in soda, and in concentrated, but not in dilute, hydrochloric acid; if the acid solution is immediately diluted, the compound is reprecipitated. When heated with glacial acetic acid, the semicarbazone yields opiazone,  $C_6H_2(OMe)_2<\begin{array}{l}CO\cdot NH\\ \quad\;\; \vert\\ CH:N\end{array}$; whilst boiling with concentrated hydrochloric acid converts the semicarbazone into normethylopiazone,  $HO\cdot C_6H_2(OMe)<\begin{array}{l}CO\cdot NH\\ \quad\;\; \vert\\ CH:N\end{array}$. *Methylic n-opianate semicarbazone*, $COOMe\cdot C_6H_2(OMe)_2\cdot CH:NH\cdot CO\cdot NH_2$, prepared from methylic *n*-opianate and semicarbazide, crystallises in needles, melts at 204°, and is insoluble in cold soda. Ethylic ψ-opianate slowly reacts with semicarbazide, and yields opianic acid semicarbazone (see above); evidently the salt is slowly hydrolysed by the water, and the free acid then condenses with the carbazide.

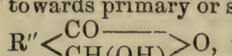
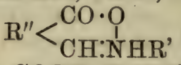
*Phthalaldehydic acid semicarbazone*, $COOH\cdot C_6H_4\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2$, prepared, like the opianic derivative, from phthalaldehydic acid, crystallises in needles, melts at 202°, dissolves in cold soda, and when boiled with glacial acetic acid, is converted into phthalazone.

Opianic acid and phthalaldehydic acid combine in alcoholic solution, with various primary and secondary bases. The resulting compounds crystallise readily, are insoluble in soda at the ordinary temperature, and are resolved into their components when boiled with baryta water, and by the action of alcoholic, and generally of aqueous, hydrogen chloride, the latter giving first yellow compounds. *Opianic acid α-naphthylamide*,  $C_6H_2(OMe)_2{<}\substack{CO\\CH(NH\cdot C_{10}H_7)}{>}O$, melts and decomposes at 212°. The *β-naphthylamide* melts at 213°, dissolves, and gives an orange-red coloration with concentrated sulphuric acid, and, by the prolonged action of soda (10—15 per cent.), is converted into the *sodium* salt, $COONa\cdot C_6H_2(OMe)_2\cdot CH{:}N\cdot C_{10}H_7$, which crystallises in long plates; the free *opian-β-naphthylamic acid*, prepared by the cautious addition of acetic acid to the sodium salt, is unstable, and melts and decomposes at 195—200°. Hydrochloric acid gives a yellow coloration, which rapidly disappears, probably indicating the formation of a hydrochloride, subsequent additions of acid momentarily restore the colour, and, finally, the greater portion of the substance dissolves. The *methylic* salt, $COOMe\cdot C_6H_2(OMe)_2\cdot CH{:}NC_{10}H_7$, is prepared from methylic *n*-opianate and *β*-naphthylamine; it crystallises in plates, and melts at 131°. The *ethylanilide*,



$$C_6H_2(OMe)_2{<}\substack{CO\\CH(NEtPh)}{>}O,$$

crystallises in plates, melts at 116—117°, and, by the action of ammonia, is resolved into its components. The *tetrahydroquinolide*,  $C_6H_2(OMe)_2{<}\substack{CO\\CH(C_9NH_{10})}{>}O$, is sparingly soluble, and melts at 180°. The *tetrahydroquinaldide*,  $C_6H_2(OMe)_2{<}\substack{CO\\CH(C_{10}NH_{12})}{>}O$, melts at 180°, gives a yellow coloration with sulphuric acid, and is only slowly decomposed by ammonia. *Phthalaldehydic acid tetrahydroquinolide*,  $C_6H_4{<}\substack{CO\\CH(C_9NH_{10})}{>}O$, crystallises in needles, and melts at 164—165°.

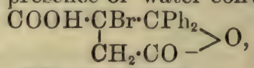
The preceding results show that towards semicarbazide, opianic acid and phthaldehydic acid react as true aldehydic acids, $COOH\cdot R\cdot CHO$; towards primary or secondary amines they react as hydroxyphthalides,  $R''{<}\substack{CO\\CH(OH)}{>}O$, if the amides are of medium basicity, but they do not react with feeble bases such as diphenylamine, nor with strong ones like piperidine, as in this case the tendency towards salt formation is too great. Tertiary amines are without action on the aldehydic acids. It is possible that when opianic acid is dissolved in alcohol, some ψ-ethylic salt is formed, but this explanation of the results is scarcely satisfactory, as the ψ-ethylic salt is without action on β-naphthylamine under the conditions described above, and the naphthylamide is formed if acetone or hot water is employed as solvent in place of alcohol. Probably the salt, $CHO{\cdot}R{\cdot}COO{\cdot}NH_3R$, is first formed, which, by condensation, is converted into the closed chain,  $R''<\begin{matrix}CO{\cdot}O\\ CH{:}NHR'\end{matrix}$, and then from this by the action of alkali, the salt $COONa{\cdot}R{\cdot}CH{:}NR$, is produced. This is in accordance with the behaviour of the β-naphthylamide, and explains the difference between the primary and secondary amines; it is possible that the formulæ given above for the amides may require amendment in this sense. J. B. T.

**Ethylic 2 : 4 : 6-Trinitrophenylmalonate.** By C. Loring Jackson and J. I. Phinney (*Ber.*, 1895, **28**, 3066—3067).—In addition to the form that melts at 58° (not 59°, as previously stated), there is a form which crystallises differently and melts at 64°; this can be obtained from a solution of the first form by sowing in it some of the crystals that melt at 64°. The authors have not yet been able to convert this second form into the first, nor have they succeeded in again preparing the first by the action of picryl chloride on ethylic sodiomalonate.

Ethylic trinitrophenylmalonate, $C_6H_2(NO_2)_3{\cdot}CH(COOEt)_2$, is converted by nitric acid into the white nitrite,

$$C_6H_2(NO_2)_3{\cdot}C(NO_2)(COOEt)_2,$$

melting at 109°; prolonged heating with nitric acid oxidises it to the *tartronate*, $C_6H_2(NO_2)_3{\cdot}C(OH)(COOEt)_2$, which melts at 117°; and hydrolysis with dilute sulphuric acid converts it into 2 : 4 : 6-*trinitrophenylacetic acid*, $CH_2(NO_2)_3{\cdot}CH_2{\cdot}COOH$, which melts at 161°, and, when crystallised from alcohol or water, loses carbonic anhydride and yields symmetrical trinitrotoluene. C. F. B.

**Condensation of Simple Ketones with Ethylic Succinate and with Ethylic Pyrotartrate in the presence of Sodium Ethoxide.** By Hans Stobbe (*Ber.*, 1895, **28**, 3191—3195; compare Abstr., 1895, i, 142 and 410).—In continuation of his work, the author has investigated the products formed by the condensation of benzophenone with ethylic succinate under the influence of sodium ethoxide. The chief product is *ethylic hydrogen diphenylitaconate*, $CPh_2{:}C(COOEt){\cdot}CH_2{\cdot}COOH$ or $CPh_2{:}C(COOH){\cdot}CH_2{\cdot}COOEt$; it melts at 124·5—125·5°, is not hydrolysed by boiling with hydrochloric acid, but with alkalis gives *γ-diphenylitaconic acid*, which melts and decomposes at 168—169°. A solution of bromine in chloroform has no action on the acid, but bromine in the presence of water converts it into *β-bromo-γ-diphenylparaconic acid*,  $\begin{matrix}COOH{\cdot}CBr{\cdot}CPh_2\\ CH_2{\cdot}CO-\end{matrix}>O$, which melts at 166·5° with liberation of gas. When reduced, the bromo-acid yields diphenylparaconic acid, and, when boiled with water, the corresponding aconic acid.

No acid isomeric with diphenylitaconic acid could be isolated from the products of the action of benzophenone on ethylic succinate.

Benzophenone, when treated with ethylic pyrotartrate in a similar manner, gave *ethylic hydrogen α-methyl-γ-diphenylitaconate*, which melts at 143·5—144·5°. When hydrolysed, the ethylic salt yields the corresponding acid, $CPh_2{:}C(COOH)\cdot CHMe\cdot COOH$, which melts and decomposes at 179—180°. No isomeric acid was obtained.

Dibenzyl ketone and ethylic succinate, in the presence of sodium ethoxide, gave the monethylic salt of the dibasic acid,

$$C(CH_2Ph)_2{:}C(COOH)\cdot CH_2\cdot COOH.$$

The acid melts at 146—147°, and the ethylic hydrogen salt at 127·5—129°.

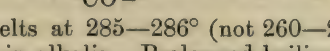
The author is at present engaged in trying to find out the constitution of the ethylic hydrogen diphenylitaconate mentioned above.

J. J. S.

**Sulphamic acids of the Aromatic Series.** By CARL PAAL and H. JÄNICKE (*Ber.*, 1895, **28**, 3160—3167; compare Abstr., 1894, i, 365).—Ammonium phenylsulphamate, $NHPh\cdot SO_3\cdot NH_4$, crystallises in white, satiny plates melting at 152°. *Orthotoluidine amidosulphonate* forms colourless prisms which melt at 131°. *Ammonium orthotolylsulphamate* crystallises in concentrically grouped, white needles which melt at 241°. *Paratoluidine amidosulphonate* forms lustrous plates melting at 139°. *Ammonium paratolylsulphamate* crystallises in lustrous, white plates melting at 215°. *Paratolylsulphamic acid*, $C_6H_4Me\cdot NH\cdot SO_3H$, crystallises in concentrically grouped, white needles which melt indefinitely at 175—190°. When the aqueous solution is heated for some time, toluidine sulphate is formed. Sodium nitrite reacts with the aqueous solution to form a white, crystalline salt, which is probably the corresponding sodium nitrosaminesulphonate. *α-Naphthylamine amidosulphonate* crystallises in lustrous plates. *Ammonium α-naphthylsulphamate* melts at 245°. *α-Naphthylsulphamic acid* crystallises in colourless, flat needles which melt and decompose at 272°. *as-Methylphenylhydrazine amidosulphonate* crystallises in lustrous, white plates melting at 106°, whilst the corresponding *ammonium methylphenylhydrazinesulphonate*, $NMePh\cdot NH\cdot SO_3\cdot NH_4$, melts at 217°. *as-Diphenylhydrazine amidosulphonate* melts at 120—121°. It has not been found possible to convert this salt into the corresponding ammonium sulphamate. *Amylamine amidosulphonate* crystallises in large, transparent tablets and melts at 185°. *Amylamine amylsulphamate*, $C_5H_{11}\cdot NH\cdot SO_3H,NH_2\cdot C_5H_{11}$, is obtained by heating the amidosulphonate with an excess of amylamine at 190—200°, and forms lustrous plates melting at 110°.

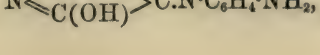
A. H.

**Isatin.** EDWARD SCHUNCK and LEO MARCHLEWSKI (*Ber.*, 1896, **29**, 194—203).—When acetylisatin is warmed with 1 : 2-phenylenediamine in alcoholic solution, *amidoacetylphenimeisatin*,

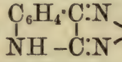


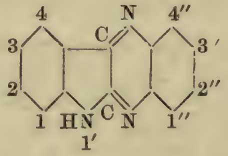
$$NAc<\begin{smallmatrix}C_6H_4\\CO-\end{smallmatrix}>C{:}N\cdot C_6H_4\cdot NH_2,$$

is formed; this melts at 285—286° (not 260—261°), and is soluble both in acids and in alkalis. Prolonged boiling with alkaline hydroxides converts it into yellow 2-*amidophenimeisatin*,



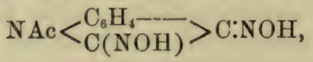
$$N<\begin{smallmatrix}C_6H_4-\\C(OH)\end{smallmatrix}>C{:}N\cdot C_6H_4\cdot NH_2,$$

which melts at 260—261°, and dissolves both in alkalis and in acids, yielding even a crystallised hydrochloride. This substance yields azo-dyes; boiling with acetic anhydride converts it into the acetyl derivative described above; and the action of acids—the mere crystallising from hot acetic acid suffices—gives rise to the formation of the substance  $\left.\begin{array}{l}C_6H_4\cdot C{:}N\\ NH-C{:}N\end{array}\right>C_6H_4$, previously obtained from isatin and 1 : 2-phenylenediamine, and called isatohydrophenazine (this vol., i, 96), but which it is now proposed to name *indophenazine;* the scheme of numbering proposed for the derivatives of indophenazine will be found adjoined.



3-*Methylindophenazine* is obtained from methylisatin and orthophenylenediamine; it is yellow, and melts at 248°; its white 1′-*acetyl derivative* melts at 204°. 1 : 3-*Dibromindophenazine,* from dibromisatin, is orange coloured, and melts at 275°; its 1′-*acetyl derivative* is yellow. *Nitroindophenazine,* from nitroisatin, is yellowish-brown, and has not melted at 305°; its *acetyl derivative* is yellow.

Acetylisatin, unlike isatin itself, yields a *dioxime,*



$$NAc<\begin{array}{l}C_6H_4\text{———}\\ C(NOH)\end{array}>C{:}NOH,$$

which melts and decomposes at 240°. C. F. B.

### Displacement of Isodiazo-groups by Cyclic Radicles. II.

By Otto Kühling (*Ber.*, 1896, **29**, 165—169; compare Abstr., 1895, i, 182 and 290).—The author finds that in the paranitrophenylpyridine, described in his previous paper (*loc. cit.*), the nitrophenyl group is in the α- and not in the γ-position as stated.

Sodium nitrophenylnitrosamine and nitrobenzene react in the presence of acetic acid to form 4 : 4′-dinitrodiphenyl (m. p. 233°; compare Fittig, *Annalen*, **124**, 276) and 2 : 4′-dinitrodiphenyl. The nitrophenyltoluene, of melting point 103—104° (compare Bamberger and also Kühling, Abstr., 1895, i, 182, 289), is probably the diparacompound, and the oily isomeride probably the orthopara-compound.

*Paranitrophenylbenzoic acid,* [? 4′ : 4], is obtained on oxidising the solid nitrophenyltoluene with excess of potassium permanganate; it crystallises in colourless needles, melts at 222—225°, and is only sparingly soluble in water, but readily in hot alcohol. When reduced with tin and hydrochloric acid, it yields *paramidophenylbenzoic acid hydrochloride.* The *free acid,* $NH_2\cdot C_6H_4\cdot C_6H_4\cdot COOH$ [? 4′ : 4], crystallises in small needles or thin plates, melts and decomposes at 106—110°, and is only sparingly soluble in hot water.

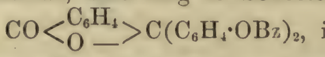
*Paramido-α-phenylpyridine hydrochloride,* $NH_2\cdot C_6H_4\cdot C_5NH_4,2HCl$, obtained by the reduction of the corresponding nitro-compound, forms a colourless, microcrystalline powder, and the *picrate* crystallises in yellow prisms which melt at 210°. The *base* itself crystallises in small, white plates which rapidly turn red, and melts at 101—102°. When the hydrochloride, in alcoholic solution, is treated with sodium nitrite, it yields 2-phenylpyridine (compare Skraup and Cobenzl, Abstr., 1883, 1015). Sodium nitrophenylnitrosamine and quinoline condense in the presence of acetic acid to form *paranitrophenylquinoline*, which separates from its alcoholic solution in the form of yellow, crystalline aggregates, and melts at 158—160°. It is soluble in strong acids, yielding yellow solutions.

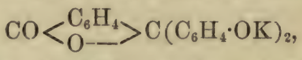
*Paranitrophenylnaphthalene*, obtained by a similar method, crystallises in bright orange needles, melts at 129°, and is practically insoluble in water, but readily soluble in ether. J. J. S.

**Formation of Phenylparatolylmethane by the Action of Sodium on Parabromotoluene.** By MAX WEILER (*Ber.*, 1896, **29**, 111—114).—When parabromo- or pariodo-toluene is treated with sodium, a certain amount of toluene is produced along with hydrocarbons of high boiling point, two substances being formed, one of which is identical with paraditolyl. The second has not yet been obtained pure; it is contained in the fraction boiling at 286—293°, and yields paratoluic acid when oxidised with excess of chromic anhydride. If, however, it is oxidised with the calculated amount of chromic anhydride, it is converted into a ketone, which yields an oxime melting at 145—150°, and is probably paratolyl phenyl ketone. The second hydrocarbon must, therefore, be phenylparatolylmethane.
A. H.

**Phthaleïns.** By JOSEF HERZIG and HANS MEYER (*Ber.*, 1895, **28**, 3258—3261).—By the action of methylic iodide on phenolphthaleïn in alkaline solution, 85—90 per cent. of the lactone dimethylic ether is formed; this is scarcely compatible with Friedländer's formula for the sodium salt. Several theories of its formation are discussed; at present, the authors, following von Baeyer, suggest that the decolorisation of phenolphthaleïn solution by means of alkali in excess, is due to the formation of a salt of the acid $C_{20}H_{16}O_5$; the regeneration of the colour, when the liquid is heated, being caused by the dissociation of this salt. Friedländer has described the acetyl derivative of phenolphthaleïn oxime as insoluble in alkali; but this is inconsistent with his formula for it; the substance prepared by him appears to be a mixture of two or three compounds, and is being further investigated. Quinoïdal fluoresceïn ethyl ether yields a *monacetyl* derivative which crystallises in highly coloured, yellowish-brown needles melting at 188—190°. Nietzki and Schroeter prepared yellow fluoresceïn ethylic ether by the hydrolysis of the quinoïdal diethylic derivative, and found that it gives a colourless, acetyl compound; this work has been repeated, and it is found that both the diethylic and ethylic acetyl derivatives, when treated with alcoholic potash and acidified, give a yellow precipitate, the supernatant liquid being fluorescent. On extraction with ether, the solid dissolves, and, after the ether is removed, a white, somewhat unstable compound is obtained; this gradually becomes yellow by repeated recrystallisation, but the change is more rapid when the substance is heated, and, at 250°, it melts, forming an orange-coloured liquid. The subject is being further investigated. J. B. T.

**Phthaleïns.** By JOSEF HERZIG and HANS MEYER (*Ber.*, 1896, **29**, 138—139).—In their preceding paper, the authors failed to mention that Haller and Guyot (Abstr., 1895, i, 376) had already obtained the lactone diethyl ether of phenolphthaleïn. The authors do not agree with those authors' views as to the quinoïdal constitution of the alkali salts of the phthaleïns. J. J. S.

**Constitution of the Alkali Salts of Phenolphthaleïn.** By AUGUSTIN BISTRZYCKI and K. NENCKI (*Ber.*, 1896, **29**, 131—132).—When phenolphthaleïn is dissolved in aqueous potash and treated with benzoic chloride, according to Schotten's method, *dibenzoylphenolphthaleïn*,  $CO{<}\genfrac{}{}{0pt}{}{C_6H_4}{O\text{—}}{>}C(C_6H_4\cdot OBz)_2$, is formed. It crystallises from benzene with 1 mol. of the solvent, in small, colourless prisms, melts when pure at 169°, and is insoluble in dilute alkalis. The potassium salt derived from phenolphthaleïn, therefore, reacts in aqueous solution as though it had the formula



$$CO{<}\genfrac{}{}{0pt}{}{C_6H_4}{O\text{—}}{>}C(C_6H_4\cdot OK)_2,$$

and not the alternative quinoïdal formula,

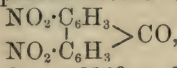
$$O{:}C_6H_4{:}C(C_6H_4\cdot OK)\cdot C_6H_4\cdot COOK,$$

suggested by Bernthsen. A. H.

**Diphenylene Ketone and Pseudodiphenylene Ketone.** By WILHELM KERP (*Ber.*, 1896, **29**, 228—233).—The author has investigated the red compound (pseudophenylene ketone) obtained, together with phenylene ketone, on distilling calcium diphenate (Fittig, *Annalen*, **166**, 373; **193**, 117; Schmidt and Schultz, *ibid.*, **207**, 345). The distillate forms a yellowish-red, crystalline mass of the formula $C_{12}H_8{:}CO$. The two compounds may be separated by means of dilute alcohol; the red compound crystallises from its ethereal solution in dark red, compact crystals, melts at 85°, and has the same percentage composition as diphenylene ketone (m. p. 83—84°). Both have the same molecular weight, and the pseudo-ketone can readily be converted into the ordinary ketone either by exposure to direct sunlight for several hours, or by treatment with boiling dilute alcohol, steam, or warm sodium ethoxide. In all these decompositions, however, a second red compound is formed, but only in very small quantities; it is still solid at 250°, and is insoluble in alcohol, ether, acids, and alkalis. If heated with alcohol at 300°, the pseudo-ketone is converted into fluorene alcohol. Both the ketone and pseudo-ketone yield the same fluorene alcohol on reduction; they also give the same oximes, and on fusing with potash the same phenylbenzoic acid; these results are, beyond doubt, due to the conversion of the pseudo-ketone into the ordinary ketone.

On treatment with zinc chloride, the oxime, which melts at 195°

(Spiegler, Abstr., 1884, 1182, 192°), yields phenanthridone (Pictet, *Chem. Zeit.*, 1894, 1822), and on reduction is converted into *diphenylenemethylamine*, $C_{12}H_{18}\colon CH\cdot NH_2$; the latter crystallises in colourless needles, melts at 161°, and is moderately soluble in warm water. Ammonium formate reduces both ketones, yielding a mixture of hydrocarbons, among which are, probably, diphenyl and fluorene. According to Schultz (*Annalen*, **203**, 103), the ordinary ketone yields a mononitro-derivative when treated with cold, fuming, nitric acid and a dinitro-derivative (m. p. 290°) with warm acid; the author shows that the pseudo-ketone with ice cold nitric acid yields a *dinitro-derivative*,



$\begin{matrix} NO_2\cdot C_6H_3 \\ | \\ NO_2\cdot C_6H_3 \end{matrix}\!>CO$, which crystallises in small, yellowish needles, melts at 310°, and is insoluble in most solvents.

J. J. S.

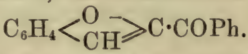
**Hydroxybenzylideneacetophenone. (Phenyl Orthohydroxystyryl Ketone).** By HERMANN BABLICH and STANISLAUS VON KOSTANECKI (*Ber.*, 1896, **29**, 233—236).—*Orthohydroxybenzylideneacetophenone* is best obtained by dissolving salicylaldehyde (1 part) and acetophenone (1 part) in alcohol (6 parts), and then treating with sodium hydroxide (1 part) dissolved in a small quantity of water. After 24 hours, the mixture is poured into water, when orthohydroxybenzylidenediacetophenone (see next page) is thrown down; orthohydroxybenzylideneacetophenone remains in solution as its sodium salt, and may be precipitated on the addition of acid; after thoroughly washing, and recrystallising from alcohol, it forms yellow plates, and melts and decomposes at 153—155°. It dissolves in dilute sodium hydroxide, yielding a yellowish-red solution, and, on adding concentrated alkali to this, the *sodium salt* separates in the form of orange-coloured needles.

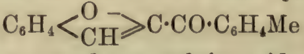
The *acetyl derivative*, $OAc\cdot C_6H_4\cdot CH\colon CH\cdot COPh$, crystallises in small plates, and melts at 68—69°; when dissolved in chloroform, it readily takes up two atoms of bromine, forming *orthacetoxybenzylideneacetophenone dibromide*, which is sparingly soluble in alcohol, crystallises in colourless prisms, and melts at 134—135°.

*Metahydroxybenzylideneacetophenone* crystallises in colourless plates, melts at 159—160°, and is readily soluble in alcohol, benzene, and chloroform, somewhat more sparingly in carbon bisulphide; its *acetyl derivative* melts at 102—103°, and the *dibromide* of the latter at 170—171°. The dibromide can be reconverted into metacetoxybenzylidene acetophenone by treatment with copper powder.

*Parahydroxybenzylideneacetophenone* forms yellowish crystals, melts at 182—183·5°, and dissolves in dilute alkali, yielding a deep yellow solution. Its *acetyl derivative* melts at 129—131°, and the *dibromide* of this at 148°.

J. J. S.

**Phenyl α-Coumaryl Ketone.** By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1896, **29**, 237—239).—When orthacetoxybenzylideneacetophenone dibromide (see preceding abstract) is dissolved in alcohol, the warm solution treated with strong potash solution, and then poured into water, a crystalline precipitate is obtained. This has the composition $C_{15}H_{10}O_2$, distils at 360° without decomposition, melts at 91°, and dissolves in concentrated sulphuric acid, yielding a yellow, non-fluorescent solution; when fused with potash, it yields coumarone and benzoic acid, $C_{15}H_{10}O_2 + H_2O = C_8H_6O + C_6H_5{\cdot}COOH$, its constitution is, therefore, that of *phenyl α-coumaryl ketone*,  $C_6H_4{<}\begin{matrix}O\,-\\CH\end{matrix}{>}C{\cdot}COPh$.

*Paratolyl orthohydroxystyryl ketone*, $OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4Me$, may be obtained from salicylaldehyde and methyl paratolyl ketone in the same way as orthohydroxybenzylidene acetophenone from salicylic aldehyde and acetophenone (see preceding abstract); it forms yellowish plates, melts at 152°, and is soluble in alkalis and concentrated sulphuric acid. Its *acetyl derivative* melts at 112°, and the dibromide of this at 136—137°. The latter compound, when dissolved in alcohol and treated with concentrated potash, yields *paratolyl α-coumaryl ketone*,  $C_6H_4{<}\begin{matrix}O\,-\\CH\end{matrix}{>}C{\cdot}CO{\cdot}C_6H_4Me$; this melts at 96°, and yields coumarone and paratoluic acid when fused with potash.

J. J. S.

**Action of Aldehydes on Ketones.** By ARNOLD CORNELSON and STANISLAUS VON KOSTANECKI (*Ber.*, 1896, **29**, 240—244; compare Schmidt, Abstr., 1881, 573, Claisen and Ponder, Abstr., 1884, 1166).—In the condensation of salicylaldehyde with acetone or with acetophenone, it is necessary to use a much more concentrated solution of sodium hydroxide than in the usual condensations of aldehydes with ketones. With acetophenone and salicylaldehyde, besides the orthohydroxybenzylideneacetophenone (compare Bablich and Kostanecki, preceding page), the authors have obtained a second compound which crystallises from alcohol in colourless needles, and is quite insoluble in alcohol, the amount formed increasing with the amount of alkali used in the condensation. It can also be obtained by the action of acetophenone (1 mol.) on orthohydroxybenzylideneacetophenone in the presence of alkali, and is, beyond doubt, *orthohydroxybenzylidenediacetophenone*, $OH{\cdot}C_6H_4{\cdot}CH(CH_2{\cdot}COPh)_2$. It is best prepared by the action of salicylaldehyde (1 part) on acetophenone (2 parts) dissolved in alcohol (10 parts), and then adding a solution of 2 parts of sodium hydroxide in 2 parts of water. After recrystallisation from alcohol, it forms thin prisms, which melt at 131°; it is readily soluble in alcohol, benzene, and chloroform, but insoluble in alkalis. When boiled with an alkali, it is decomposed into acetophenone and salicylaldehyde. Its *acetyl derivative*,

$$OAc{\cdot}C_6H_4{\cdot}CH(CH_2{\cdot}COPh)_2,$$

crystallises in colourless needles, and melts at 83—84°.

*Orthohydroxybenzylidenebismethylparatolyl ketone*,

$$OH{\cdot}C_6H_4{\cdot}CH(CH_2{\cdot}CO{\cdot}C_6H_4Me)_2,$$

was obtained as a bye-product in the preparation of paratolyl hydroxystyryl ketone (compare Kostanecki and Tambor, preceding abstract). It crystallises in colourless prisms, and melts at 131—132° its *acetyl derivative* melts at 95°.

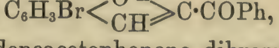
*Bromorthohydroxybenzylidenediacetophenone*,

$$OH\cdot C_6H_3Br\cdot CH(CH_2\cdot COPh)_2\ [OH : Br = 2 : 5],$$

is formed as a bye-product in the preparation of bromorthohydroxybenzylideneacetophenone (compare Kostanecki and Oppelt, following abstract); it crystallises in colourless needles, and melts at 158—159°; its *acetyl derivative* melts at 107°. J. J. S.

**Derivatives of Orthohydroxybenzylideneacetophenone (Phenyl Orthohydroxystyryl Ketone).** By Stanislaus von Kostanecki and Eugen Oppelt (*Ber.*, 1896, **29**, 244—249).—5 : 2-*Bromohydroxybenzylideneacetophenone*, $OH\cdot C_6H_3Br\cdot CH{:}CH\cdot COPh$, is obtained by the action of bromosalicylaldehyde (8 parts) on acetophenone (5 parts) in the presence of an alkali. A small quantity of the corresponding diacetophenone is formed at the same time (compare preceding abstract). It crystallises from its alcoholic solution in yellowish plates, melts and decomposes at 168°, and is soluble in both alkalis and strong sulphuric acid. The *sodium salt* is readily soluble in water, but, on the addition of more alkali, separates out in the form of glistening, red needles. The *acetyl derivative*, obtained by the action of acetic anhydride and anhydrous sodium acetate, forms glistening needles, melts at 133·5—135°, and yields a *dibromide* which melts at 158—160°.

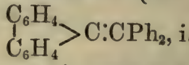
5 : 2-*Bromethoxybenzylideneacetophenone*, $OEt\cdot C_6H_3Br\cdot CH{:}CH\cdot COPh$, may be obtained by boiling an alcoholic solution of the bromhydroxy-compound with ethylic iodide and potassium hydroxide; it may also be obtained from *bromethoxybenzylideneacetophenone dibromide*, by treating it with a paste of freshly precipitated metallic copper, but is best prepared from the ethylic ether of salicylic acid and acetophenone under the influence of an alkali. It forms yellowish needles, melts at 98—100°, and is readily soluble in warm alcohol. The dibromide may be obtained either by the addition of two atoms of bromine to the ketone, or by the action of bromine on a solution of the crude ethylic ether of orthohydroxybenzylideneacetophenone in carbon bisulphide. It crystallises in plates, and melts at 165°.

*Orthobromophenyl α-coumaryl ketone*,  $C_6H_3Br{<}\begin{array}{c}O-\\CH\end{array}{\geqslant}C\cdot COPh$, is obtained when the bromacetoxybenzylideneacetophenone dibromide is suspended in warm alcohol and then treated with concentrated alkali. It crystallises in yellowish needles, and melts at 136—138°.

J. J. S.

**Action of Diphenylene Di-isocyanate on Amido-compounds.** By H. Lloyd Snape (*Chem. News*, 1896, **73**, 37).—When diphenylene dicyanate, obtained by heating benzidine hydrochloride in a current of phosgene gas, is treated in ethereal solution with gaseous ammonia, it yields diphenylenedicarbamide (H. Schiff, Abstr., 1878, 669); whilst, if an ethereal solution of aniline is used, diphenyldiphenylenedicarbamide is formed, identical with that produced from benzidine and phenylic isocyanate (B. Kühn, Abstr., 1885, 979).

D. A. L.

**Diphenyldiphenylene-ethylene.** By VICTOR KAUFMANN (*Ber.*, 1896, **29**, 73—76).—*Diphenyldiphenylene-ethylene*,  $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!>C{:}CPh_2$, is obtained by heating benzophenone chloride and fluorene in molecular proportion at 320—330° for 5—10 minutes; it melts at 229·5°, and crystallises from benzene in colourless leaflets or needles containing the solvent. Reduction of the amylic alcohol solution with sodium amalgam gives rise to *diphenyldiphenylene-ethane*, which crystallises from benzene in leaflets containing 2 mols. of the solvent; it melts at 217—218°. The *picrate* of diphenyldiphenylene-ethylene crystallises from benzene in yellow needles, and melts at 198°.

M. O. F.

**Behaviour of Stilbene Dibromide and of Tolane Dibromide with Sodium Benzenesulphinate and Sodium Phenylmercaptide.** By ROBERT OTTO (*J. pr. Chem.*, 1896, [2], **53**, 1—19; compare Abstr., 1895, i, 286, 485).—Neither stilbene dibromide nor the corresponding tolane derivative is converted into a sulphone by sodium benzenesulphinate; instead, stilbene dibromide yields stilbene, and β-tolane dibromide yields tolane; tolane and benzil were obtained when α-tolane dibromide was employed. Stilbene and tolane are the products of the action of sodium phenylmercaptide on the aforesaid dibromides.

A. G. B.

**Connection between Colour and Constitution in the Triphenylmethane Dyes.** By WILHELM VAUBEL (*J. pr. Chem.*, 1896, [2], **53**, 47—48; compare Abstr., 1895, i, 55—56).—The author defends his views concerning the relation of the colour of triphenylmethane dyes and their constitution against the criticism of Richard Meyer in the *Jahrbuch der Chemie*, 1894.

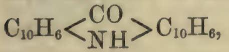
A. G. B.

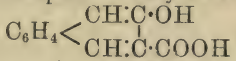
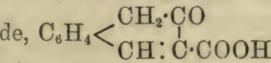
**Hydrocarbons of High Molecular Weight produced by the action of Sodium on Bromobenzene.** By MAX WEILER (*Ber.*, 1896, **29**, 115—118; compare this vol., i, 237).—The formation of hydrocarbons of high molecular weight appears to be a normal accompaniment of the action of sodium on brominated aromatic hydrocarbons. The product of the action of sodium on bromobenzene yields a series of compounds which boil above 342°, and of which the molecular weight exceeds 200. A number of crystalline substances has been isolated from the various fractions, but no attempt has yet been made to ascertain the constitution of the products.

A. H.

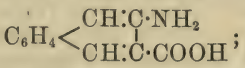
**1:2:3-Dihydroxynaphthoic acid.** By RICHARD MÖHLAU and FELIX KRIEBEL (*Ber.*, 1895, **28**, 3089—3096; compare Abstr., 1894, i, 138).—1-Naphthaleneazo-2-hydroxy-3-naphthoic acid forms deep red crystals with a greenish-yellow surface lustre, and decomposes at 182°. 1 : 2 : 3-amidohydroxynaphthoic acid forms yellow, rhombic prisms, and decomposes at 205·5°; it can also be obtained by reducing von Kostanecki's 1 : 2 : 3-nitrosohydroxynaphthoic acid (Abstr., 1894, i, 91) with stannous chloride. 1 : 2 : 3-Dihydroxynaphthoic acid melts and decomposes at 220·5° (not at 207°); its yellow *ethylic* and methylic salts melt respectively at 84—84·5° and at 95—96° (for the latter substance compare Gradenwitz, Abstr., 1894, i, 605). When this acid is oxidised with nitric acid of sp. gr. 1·2, it yields 1 : 2-*naphthaquinone-3-carboxylic acid*, which crystallises in orange-red monoclinic prisms, and decomposes at 154°; its methylic salt, prepared by oxidation of the corresponding dihydroxy salt, is orange-red, and begins to decompose at 121°, melting at 139—140° (compare Gradenwitz, *loc. cit.*).

C. F. B.

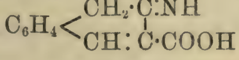
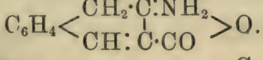
**2 : 3-Amidonaphthoic acid.** By RICHARD MÖHLAU (*Ber.*, 1895, **28**, 3096—3099; compare Abstr., 1894, i, 138).—This acid is best obtained by heating the sodium salt of the corresponding hydroxy-acid with ammonia in an autoclave at 260—280°; it melts at 214°, (not at 211—212°); the colourless 2-*acetamido-derivative* melts at 238°, the yellow *methylic salt* at 115—115·5. When a mixture of 2 : 3-amidonapthoic and 2 : 3-hydroxynaphthoic acids with ammonia and zinc chloride is heated at 260—280°, a yellow *dinaphthacridone*,  $C_{10}H_6{<}\begin{array}{c}CO\\ NH\end{array}{>}C_{10}H_6$, melting above 300°, is formed. C. F. B.

**Constitution of 2 : 3-Hydroxynaphthoic acid and its Derivatives.** By RICHARD MÖHLAU (*Ber.*, 1895, **28**, 3100—3101).—2 : 3-Hydroxynaphthoic acid is coloured and so are its salts, but when the hydroxylic hydrogen is replaced, colourless compounds are formed. The same is true of the hydroxy-, amido-, and sulphonic derivatives of this acid. The colourless compounds may be regarded as derived from the true hydroxy-acid,  $C_6H_4{<}\begin{array}{l}CH{:}C{\cdot}OH\\ \quad\ \ \vert\\ CH{:}C{\cdot}COOH\end{array}$; the coloured ones from the desmotropic isomeride,  $C_6H_4{<}\begin{array}{l}CH_2{\cdot}CO\\ \qquad\ \vert\\ CH{:}\,C{\cdot}COOH\end{array}$.

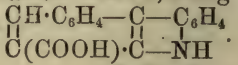
In the same way, the colourless salts of 2 : 3-amidonaphthoic acid are to be regarded as derived from the normal acid,



$$C_6H_4{<}\begin{array}{l}CH{:}C{\cdot}NH_2\\ \quad\ \ \vert\\ CH{:}C{\cdot}COOH\end{array};$$

the acid itself and its salts, being coloured yellow, from the desmotropic form,  $C_6H_4{<}\begin{array}{l}CH_2{\cdot}C{:}NH\\ \qquad\ \vert\\ CH{:}\,C{\cdot}COOH\end{array}$ or  $C_6H_4{<}\begin{array}{l}CH_2{\cdot}C{:}NH_2\\ \qquad\ \vert\\ CH{:}\,C{\cdot}CO\end{array}{>}O$.

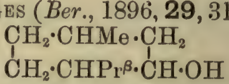
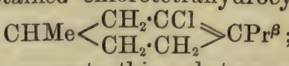
C. F. B.

**Constitution of 2 : 3-Hydroxynaphthoic acid.** By MARTIN SCHÖPFF (*Ber.*, 1896, **29**, 265—270).—Möhlau has recently suggested (preceding abstract) that 2 : 3-hydroxynaphthoic acid is really a keto-derivative [$CH_2$ : CO : COOH = 1 : 2 : 3]; the author reached the same conclusion some time ago, chiefly from a study of the action of phenylhydrazine on the acid. When heated at 130—140°, they combine, ammonia, water, and *phenylnaphthylcarbazolecarboxylic acid*, $C_{17}H_{11}NO_2$, being formed; the latter crystallises in yellowish-green needles, melts at 325°, and is very sparingly soluble. The *ethylic* salt crystallises in yellow needles, melting at 175°. The *sodium* salt is deposited in silvery, lustrous plates, and becomes yellow at 100°. The *barium*, *magnesium*, and *calcium* salts are yellow and sparingly soluble. The *acetyl* derivative is crystalline, insoluble in alkali, and remains unmelted at 350°. *Phenylnaphthylcarbazole* is formed by distilling the acid with zinc dust in a current of hydrogen; it crystallises from light petroleum, melts at 120°, and, in solution, has a blue fluorescence; a pine splinter, treated with the carbazole and then with hydrogen chloride, is coloured violet. The *picrate* is crystalline. The *nitroso*-derivative crystallises in small, yellow needles, melts at 132°, gives Liebermann's reaction, and produces a green coloration with concentrated sulphuric acid. The *acetyl* derivative crystallises in silvery, lustrous plates, and melts at 142°. The *benzoyl* derivative is deposited in slender, colourless needles, melting at 170°. The reaction between phenylhydrazine and the naphthoic acid probably takes place in two stages, a hydrazone, $COOH\cdot C_{10}H_7{:}N\cdot NHPh$, being first formed, and then the carbazolecarboxylic acid,  $\begin{array}{l} CH\cdot C_6H_4-C-C_6H_4 \\ C(COOH)\cdot C-NH \end{array}$.

J. B. T.

**Some 1 : 2′-Derivatives of Naphthalene.** By PAUL FRIEDLAENDER and S. ZINBERG (*Ber.*, 1896, **29**, 37—42).—The *sodium hydrogen* and *barium hydrogen salts*, both with $6H_2O$, of hydroxydisulphonaphthoic acid [$OH : COOH : (SO_3H)_2 = 1 : 2 : 4 : 2'$] (König, Abstr., 1889, 719) are described. When the acid is fused with sodium hydroxide at 220—240°, it is converted into 1 : 2′ : 4-*dihydroxysulpho-2-naphthoic acid*, the *sodium hydrogen*, and *acid aniline salts* of which were prepared; heating with 50 per cent. sulphuric acid at 140° converts this acid into 1 : 2′-*dihydroxy-2-naphthoic acid*, which melts and decomposes at 217°, and the *barium salt* of which crystallises with $4H_2O$. The latter acid, when boiled with aniline, yields 1 : 2′-dihydroxynaphthalene (Emmert, Abstr., 1888, 57), melting at 175°; concentrated aqueous ammonia converts it at 200—210° into 1 : 2′-naphthylenediamine; at 170—180° into 2′ : 1-amidonaphthol (Abstr., 1892, 1234), the *acetyl derivative* of which melts at 210—211°. The isomeric 1 : 2′-amidonaphthol was prepared by heating 1 : 2′-naphthylaminesulphonic acid with sodium hydroxide at 250—260°; it forms pale, brownish needles, and decomposes above 200°; its *acetyl derivative* melts at 165°.

C. F. B.

**Menthol.** By ERNST JÜNGER and A. KLAGES (*Ber.*, 1896, **29**, 314—318).—In order to establish the formula  $\begin{array}{l} CH_2\cdot CHMe\cdot CH_2 \\ CH_2\cdot CHPr^{\beta}\cdot CH\cdot OH \end{array}$ for menthol (compare Abstr., 1893, i, 359), the authors have converted menthone into dichlorohexahydrocymene, and by elimination of hydrogen chloride obtained chlorotetrahydrocymene, which probably has the constitution  $CHMe<\begin{array}{l} CH_2\cdot CCl \\ CH_2\cdot CH_2 \end{array}>CPr^{\beta}$; treatment with bromine and quinoline converts this substance into 3-chlorodihydrocymene, from which 3-chlorocymene is obtained, the chlorine atom occupying the position originally assumed by the hydroxyl group in menthol. In order to identify the cymene derivative thus obtained, the two chlorocymenes have been prepared and characterised.

2-*Chlorocymene* is produced by the chlorination of cymene obtained from camphor; it boils at 117·5° under a pressure of 35 mm., and at

214—216° under atmospheric pressure. The sp. gr. = 1·017, and the refractive index $n_D = 1·51118$ at 17°.

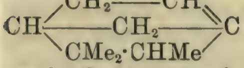
2-*Chlorocymene*-5-*sulphonic acid* crystallises from benzene in colourless needles, and melts at 135—136°; the *barium* salt crystallises in leaflets which contain water, and the *chloride*, *amide*, and *anilide* melt at 68—69°, 191—192°, and 181° respectively.

3-Chlorocymene is obtained by the action of phosphorus pentachloride on thymol; it boils at 214°, has sp. gr. = 1·018, and the refractive index $n_D = 1·51796$. The *sulphonamide* crystallises from dilute alcohol in nacreous leaflets, and melts at 168°; the *barium* salt of the sulphonic acid crystallises in needles, and contains $4H_2O$.

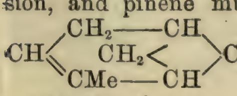
Chlorotetrahydrocymene, $C_{10}H_{17}Cl$, is produced by the action of phosphoric chloride on menthone (Abstr., 1892, 867), and quinoline converts its bromo-derivative into *chlorodihydrocymene*, $C_{10}H_{15}Cl$, which boils at 112° under a pressure of 35 mm., and 212° under atmospheric pressure; this substance has the sp. gr. = 0·990, and the refractive index $n_D = 1·49712$. Treatment of chlorodihydrocymene with bromine (1 mol.), and distillation of the product with quinoline, yields 3-chlorocymene, in every respect identical with the substance already described.

Hexahydrocymene, which is readily produced by the addition of sodium to an alcoholic solution of chlorohexahydrocymene (menthylic chloride), is identical with menthonaphthene, described by Berkenheim (Abstr., 1892, 866), and also with the menthane of Wagner (Abstr., 1894, i, 469). M. O. F.

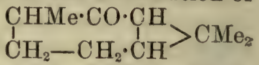
**Orientation in the Terpene Series: Carone and Pinene.** By Adolf von Baeyer (*Ber.*, 1896, **29**, 3—26; compare Abstr., 1895, i, 549).—The evidence afforded by Wagner (Abstr., 1894, i, 469), and more recently by Wallach (Abstr., 1895, i, 547), in favour of representing terpineol by the formula $\mathrm{CMe}<\begin{smallmatrix}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{smallmatrix}>\mathrm{CH\cdot CMe_2\cdot OH}$, has demanded a re-modelling of the author's system of orientation in regard to almost all members of the terpene series excepting those of the terpinolene group. Whilst admitting the accuracy of Wagner's formulæ for terpineol, terpin, limonene, carvone, and dihydrocarvone, Tiemann and Semmler regard pinene as having the constitution



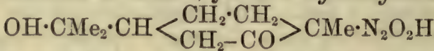
(Abstr., 1895, i, 428), basing this hypothesis on the behaviour of pinonic acid towards oxidising agents (Abstr., 1895, i, 477). The author, however, has oxidised pinene in the manner indicated by these investigators, and obtained pinonic acid in a form which, although having the empirical formula $C_{10}H_{16}O_3$, and boiling at the temperature observed by them, becomes crystalline very readily, and, on oxidation with alkali hypobromite, yields a dibasic acid of the composition $C_9H_{14}O_4$, to which he refers as pinic acid. This behaviour is not in agreement with the foregoing expression, and pinene must, therefore, be represented by the formula



already advocated by Wagner (*loc. cit.*).

The production of hydrobromodihydrocarvone and hydroxytetrahydrocarvone, by the addition of the elements of hydrogen bromide and of water to carone, meets with explanation if the constitution of the latter substance is expressed by the formula  $\left.\begin{matrix}\mathrm{CHMe\cdot CO\cdot CH}\\ \mathrm{CH_2{-}CH_2\cdot CH}\end{matrix}\right>\mathrm{CMe_2}$ (compare Abstr., 1895, i, 551); this view removes the author's objection to Bredt's formula for camphor, which he now regards as more probable than the expression advocated by Tiemann (Abstr., 1895, i, 428).

The conversion of carvone, limonene, terpineol, pinene, nitrosopinene, and isocarvoxime into hydrochlorocarvoxime by a method described in the present paper, is regarded as justifying the classification of these substances in one natural group.

It has been already mentioned that hydroxytetrahydrocarvone is formed by the addition of the elements of water to carone. Caronebisnitrosylic acid, also, when dissolved in alcohol and submitted to the action of a current of steam, yields 8-*hydroxytetrahydrocarvonebisnitrosylic acid*,  $\mathrm{OH\cdot CMe_2\cdot CH}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2{-}CO}\end{matrix}{>}\mathrm{CMe\cdot N_2O_2H_2}$, which crystallises from dilute methylic alcohol in rhombic plates, and melts and evolves gas at 184°. Glacial acetic acid saturated with hydrogen bromide converts it into *bromotetrahydrocarvonebisnitrosylic acid*,

$$\mathrm{CMe_2Br\cdot C_6H_7OMe\cdot N_2O_2H_2},$$

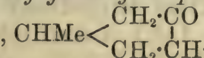
which also crystallises in rhombic plates, and melts and decomposes at 130°; treatment with alcoholic potash regenerates caronebisnitrosylic acid. *Hydroxycarone* is obtained from bisnitrosocarone dichloride and hydrobromodihydrocarvone dibromide by the action of caustic soda; it boils at 125—135° under a pressure of 20 mm., and forms a crystalline *sodium* derivative. Hydroxycarone and *ketoterpine*, obtained by agitation with sulphuric acid, will be more fully described. Oxidation of eucarvone with potassium permanganate has led to the formation of asymmetric dimethylsuccinic acid.

When the $\alpha$- and $\beta$-modifications of *d*-limonene nitrosochloride are treated with alcoholic hydrogen chloride, active hydrochlorocarvoxime is produced; the inactive modification is obtained, however, from hydrochlorodipentene nitrosochloride, terpineol nitrosochloride, pinene nitrosochloride, and nitrosopinene. The active hydrobromocarvoxime is produced when $\alpha$-dextrolimonene nitrosochloride is treated with ethereal hydrogen bromide, whilst pinene nitrosochloride and terpineol nitrosochloride yield the inactive modification; eucarvone, however, is indifferent towards this agent.

On oxidising pinene, according to the method adopted by Tiemann and Semmler (Abstr., 1895, i, 477), the chief product obtained by the author is *$\alpha$-pinonic acid*, $C_{10}H_{16}O_3$, which melts at 103—105°, and boils at 180—187° under a pressure of 14 mm.; the *oxime* crystallises in large, transparent plates or prisms, and melts at 150°, whilst the *phenylhydrazone* crystallises from dilute alcohol in lustrous, colourless leaflets, which melt and decompose below 100°. This result is not in agreement with the observations of the above-mentioned investigators, who obtained liquid pinonic acid, which boils at the same temperature as the solid modification, and yields two isomeric oximes, melting at 125° and 160° respectively. A crystalline acid which the author calls *nopic acid* is another product of the oxidation of pinene, but it is not formed when the pure hydrocarbon is employed; it is isomeric with pinonic acid, but, unlike this substance, it is not ketonic. Nopic acid melts at 125°, and the *sodium* salt is sparingly soluble in water.

Tiemann and Semmler have observed that pinonic acid is indifferent towards alkali hypobromite (*loc. cit.*); $\alpha$-pinonic acid, however, is readily oxidised by this agent, yielding *pinic acid*, $C_9H_{14}O_4$, which crystallises from water in long prisms, and melts at 101—102·5°. Pinic acid is dibasic, but does not form an anhydride under the influence of boiling acetic chloride; the solution is slowly oxidised by potassium permanganate on the water bath, but is indifferent towards it at the ordinary temperature. Hydrobromic acid has no action on pinic acid at 100°, and the aqueous solution is optically inactive. M. O. F.

**Orientation in the Terpene Series. Menthone and Tetrahydrocarvone.** By ADOLF VON BAEYER [and EUGEN OEHLER] (*Ber.*, 1896, **29**, 27—37; compare Abstr., 1894, i, 522, and 1895, i, 549).—2 : 6-Dimethyl-3-oximidoctanoic acid, the open chain acid derived from nitrosomenthone by the addition of the elements of water, melts at 103° (compare *loc. cit.*). 2 : 6-*Dimethyloctan*-3-*onoic acid*, obtained by treating it with boiling dilute acids, boils at 186—187° under a pressure of 20 mm.; the *semicarbazone* crystallises in prisms and melts at 152°.

*Isobutyrylmethylketopentamethylene* (1 : 4-*methylisobutoylcyclopentane*-3-*one*),  $CHMe\left\langle\begin{array}{l}CH_2\cdot CO\\ \quad\quad\ \ |\\ CH_2\cdot CH\cdot CO\cdot CHMe_2\end{array}\right.$, is formed when the ethylic salt of the foregoing acid is heated with sodium and xylene for three hours at 120—130°; it is a colourless oil, boiling at 115—116° under a pressure of 25 mm., and develops a red coloration in alcoholic solution with ferric chloride; the *copper* derivative crystallises in bright green, silky needles, and *compounds* are also formed with sodium hydrogen sulphite and ammonia. The *dioxime* crystallises in small needles, and melts at 144°. On heating the diketone with aqueous potash, the ketonic acid is regenerated.

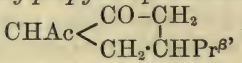
2 : 6-*Dimethyloctan*-3-*oloic acid*,

$$CHMe_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot COOH,$$

is obtained by heating 2 : 6-dimethyloctan-3-onoic acid with absolute alcohol and sodium; the *silver* salt crystallises in lustrous leaflets, and the *lactone* boils at 155—165° under a pressure of 25 mm. On oxidising the acid with potassium permanganate, $\beta$-methyladipic acid is formed.

5-*Isopropylheptan*-2-*onoic acid*, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot COOH$, is obtained by the action of amylic nitrite and hydrochloric acid on tetrahydrocarvone, the product being hydrolysed with dilute sulphuric acid; it forms colourless crystals, melting at 40°, and boils at

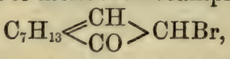
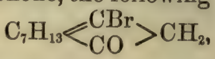
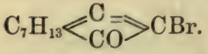
192° under a pressure of 20 mm. The *semicarbazone* melts at 152—153°, and the *oxime* at 75—78°; the *phenylhydrazone* crystallises in golden needles and melts at 102°, and the *ethylic* salt boils at 143—146° under a pressure of 12 mm.

*Acetylpropylketopentamethylene* (1 : 4-*acetylisopropylcyclopentan*-2-*one*),  $CHAc<\begin{matrix}CO-CH_2\\ \vert \quad\\ CH_2\cdot CHPr^{\beta}\end{matrix}$, is obtained from the foregoing ethylic salt by means of sodium and xylene; it is a sweet, colourless oil, which boils at 130—132° under a pressure of 25 mm. The *copper* derivative crystallises in light green needles, and the *dioxime* melts at 165°; hydrolysis of the diketone gives rise to the original acid.

When bisnitrosotetrahydrocarvone is treated with ethereal hydrogen chloride, tetrahydrocarvonebisnitrosylic acid is formed, crystallising in leaflets, which melt and decompose at 82°; the *oxime* of bisnitrosotetrahydrocarvone is also produced, and melts at 75—77°. In preparing the bisnitrosylic acid, a chlorinated ketone is formed, which yields a new *terpenone*, $C_{10}H_{16}O$, when treated with sodium acetate and acetic acid; the *semicarbazone* melts at 222—223°.

Isopropylheptanonoic acid is also formed when tetrahydrocarvone is gently oxidised with potassium permanganate; more vigorous action gives rise to isopropylsuccinic acid. M. O. F.

**The Terpenes and Camphor.** By FERDINAND TIEMANN (*Ber.*, 1896, **29**, 119—131).—The author reviews the course of his recent investigations, and discusses the changes attending the conversion of camphoroxime into campholenonitrile. In the light of von Baeyer's work (this vol., i, 246), the oily pinonic acid obtained by Tiemann and Semmler (Abstr., 1895, i, 478) on oxidising pinene is regarded as a mixture of isomerides; a similar mixture is produced when α-dihydroxydihydrocampholenic acid (m. p. 144°) is distilled, and this fact is considered favourable to the pinene formula already advocated by Tiemann and Semmler (*loc. cit.*). M. O. F.

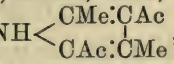
**Bromo-derivatives of the Camphor Series.** By ANGELO ANGELI and E. RIMINI (*Gazzetta*, 1895, **25**, ii, 162—164; compare Abstr., 1895, i, 382).—The authors ascribe to ordinary bromocamphor, to the isomeride melting at 113°, obtained by the action of hydrogen bromide on camphenone, and to monobromocamphenone, the following constitutions respectively:  $C_7H_{13}<\begin{matrix}CH\\ CO\end{matrix}>CHBr$,  $C_7H_{13}<\begin{matrix}CBr\\ CO\end{matrix}>CH_2$,  $C_7H_{13}<\begin{matrix}C=\\ CO\end{matrix}>CBr$. These constitutions are in agreement with Bredt's formula for camphor. W. J. P.

**Ledum-camphor.** By EDVARD I. HJELT (*Ber.*, 1895, **28**, 3087—3089).—The stearoptene contained in oil of wild marsh rosemary, obtained from the leaves of *Ledum palustre* (Abstr., 1882, 346), has the molecular formula $C_{15}H_{26}O$; Rizza's analysis had already indicated this. It is thus a camphor of the sesquiterpene series; it melts at 104—105° and boils at 282—283°; it dissolves in alcohol to the extent of 10·4 per cent. at 17·5°, and the solution is feebly dextrorotatory, $[\alpha]_j = 7{\cdot}98$; it is a poison, affecting the central nervous system. Warming with dilute sulphuric acid on the water bath suffices to make it lose water and yield the sesquiterpene *ledene*, $C_{15}H_{24}$, which is an oil boiling at 255°, and rapidly acquiring a greenish tinge. On account of the ease with which the camphor loses water, it is difficult to get the hydroxyl group to react; neither benzoic chloride nor phenylic isocyanate form derivatives, but the *chloride*, $C_{15}H_{25}Cl$, can be obtained as a yellowish oil by the action of successive small quantities of phosphorus pentachloride on a solution of the camphor in light petroleum; heating with quinoline converts this chloride into ledene.

C. F. B.

**Ammoniacum.** By H. Luz (*Arch. Pharm.*, 1895, **233**, 540—550).—The sample examined contained 4·5 per cent. of water, 69 per cent. of resin, 22·7 per cent. of substances soluble in water, and 3·5 per cent. of substances, other than resin, insoluble in water. A considerable amount of salicylic acid was present, but no aldehydes or terpenes. Normal butyric and valeric acids were also present, largely in combination with a resin alcohol, *ammoresinotannol*, $C_{18}H_{30}O_3$, a chocolate-brown, tasteless, and odourless powder, insoluble in water, but soluble in alkalis and acids. Ammoresinotannol is oxidised by nitric acid to styphnic acid. The resin consists essentially of ammoresinotannol salicylate. The *acetyl* derivative, $C_{18}H_{29}AcO_3$, is a brown powder, soluble in acetone, &c. The *benzoyl* derivative is similar. The gum of gum ammoniacum appears to contain calcium arabinate.

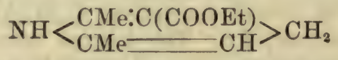
JN. W.

**Conversion of Acetylacetone into Pyrroline Derivatives.** By CARLO U. ZANETTI (*Real. Accad., Lincei*, 1893, i, 324—327).—3 : 5-*Diacetyl*-2 : 4-*dimethylpyrroline*,  $NH<\begin{matrix}CMe:CAc\\ | \\ CAc:CMe\end{matrix}$, is formed on adding potassium nitrite to a cooled acetic acid solution of acetylacetone, and then reducing the product with zinc dust; on filtering and neutralising with sodium carbonate, the base separates, and is ultimately obtained in colourless, flattened needles, melting at 136°. It is soluble in most organic solvents, and is a very feeble base; the *aurochloride*, $C_{10}H_{13}NO_2,HAuCl_4$, melts at 120—130° with previous decomposition, and is decomposed by water. On heating the base with potash and benzaldehyde, it yields 3 : 5-*dicinnamoyl*-2 : 4-*dimethylpyrroline*, $C_{24}H_{21}NO_2$, which crystallises in nodular groups of small needles, melting at 215—216°.

*Nitrosoacetylacetone*, $(COMe)_2C{:}NOH$, the intermediate product in the preparation of the above pyrroline, may be isolated by adding sulphuric acid to a potash solution of acetylacetone containing potassium nitrite, and then extracting with ether; on evaporating the ethereal solution and recrystallising, it is obtained in flattened needles or scales, melting at 75°. It is soluble in water, alcohol, or ethylic acetate, but only sparingly so in benzene or petroleum.

On heating sodioacetylacetone, suspended in ether, with iodine, a *substance*, $C_{10}H_{14}O_4$, is obtained, which melts at 186—187°, and is possibly symmetrical tetracetylethane. W. J. P.

**Synthesis of Pyridine Derivatives by the Action of Ethylic Acetoacetate on Aldehydes in Presence of Ammonia.** By Robert Schiff and P. Prosio (*Gazzetta*, 1895, **25**, ii, 65—90).—On gradually adding alcoholic ammonia to a mixture of ethylic acetoacetate and commercial formaldehyde solution, heat is generated, and Griess and Harrow's ethylic dihydrolutidinedicarboxylate, melting at 176—183° (Abstr., 1888, 1313), is slowly deposited; the action proceeds in accordance with the equation $2C_6H_{10}O_3 + H{\cdot}COH + NH_3 = C_{13}H_{19}NO_4 + 3H_2O$, and a 95 per cent. yield is obtained. The same substance is deposited immediately on adding the requisite amount of a hydrochloric acid solution of formaldehyde to a mixture of ethylic acetoacetate and alcoholic ammonia, so that the action proceeds both in acid and in alkaline solutions; the ethereal salt has neither acid nor basic properties, and, when heated with hydrochloric acid, yields ethylic lutidinedicarboxylate, melting at 72°, but no hydrogen is evolved as stated by Griess and Harrow (*loc. cit.*), the effervescence being due to carbonic anhydride and ethylic chloride. The same conversion may be effected by saturating an absolute alcoholic solution of ethylic dihydrolutidinedicarboxylate with dry hydrogen chloride, evaporating the alcohol, and adding sodium carbonate, when ethylic lutidinedicarboxylate separates. The alkaline mother liquor contains *ethylic* 2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3-*carboxylate*,



$$\mathrm{NH}{<}\begin{array}{l}\mathrm{CMe{:}C(COOEt)}\\ \mathrm{CMe{=\!=\!=\!=}CH}\end{array}{>}\mathrm{CH_2}$$

it is extracted by ether, and is ultimately obtained as a yellowish oil of coniine-like odour, which distils unchanged at 235°, and is more soluble in cold than in hot water. The *platinochloride*,

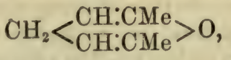
$$(C_{10}H_{15}NO_2)_2,H_2PtCl_6,$$

crystallises in yellow needles melting at 140°, and the *compound* with mercuric chloride, $C_{10}H_{15}NO_2,HgCl_2$, is a yellow powder insoluble in water. The salt is readily hydrolysed by potash yielding the corresponding acid, of which the *hydrochloride*, $C_8H_{11}NO_2,HCl$, forms small glassy crystals, whilst the *platinochloride*,

$$(C_8H_{11}NO_2)_2,H_2PtCl_6,2H_2O,$$

crystallises in small red prisms, which lose their water at 120°.

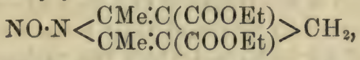
On heating ethylic dihydrolutidinedicarboxylate with alcoholic potash, ammonia is evolved, and, on adding water and extracting with ether, Knoevenagel's tetrahydroketotoluene (Abstr., 1895, i, 48), which boils at 192—197°, is obtained; it is doubtless formed by isomeric change occurring in a substance of the constitution



$$\mathrm{CH_2}{<}\begin{array}{l}\mathrm{CH{:}CMe}\\ \mathrm{CH{:}CMe}\end{array}{>}\mathrm{O},$$

which should be first produced from the dicarboxylate. The alkaline mother liquors, when exactly neutralised, deposit *lutidinedicarboxylic acid*, $C_9H_9NO_4$; this crystallises from boiling water in thin, white needles having a very high melting point, and is only sparingly soluble in alcohol or ether. The same acid may be prepared from the sodium salt obtained by the action of sodium ethoxide on ethylic lutidinedicarboxylate.

Nitric acid (sp. gr. 1·36—1·40) dissolves ethylic dihydrolutidinedicarboxylate with slight rise of temperature, and, after neutralisation, the product yields ethylic lutidinedicarboxylate crystallising in compact scales, which melt at 72° and become electrified by friction. On leaving the dihydrolutidinedicarboxylate in contact with fuming hydrochloric acid, and then neutralising with sodium carbonate, a substance is deposited which crystallises in long, lustrous needles melting at 71—72°, but which does not become electrified by friction. On recrystallisation from boiling solvents, however, this labile substance becomes converted into the above stable modification, which is easily electrified; if, however, instead of crystallising the precipitate obtained by adding carbonate, it is merely washed and dried, it is found to be an *imido-base* isomeric with the original so-called ethylic dihydrolutidinedicarboxylate, and melts at 58—60°. This base, *ethylic isodihydrolutidinedicarboxylate*, has the constitution $NH<\genfrac{}{}{0pt}{}{CMe{:}C(COOEt)}{CMe{:}C(COOEt)}>CH_2$, and is very readily oxidised by exposure to the air or by heating with alcohol, giving ethylic lutidinedicarboxylate. It readily yields a *nitroso-derivative*,

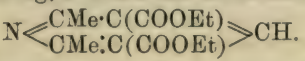


$$NO{\cdot}N<\genfrac{}{}{0pt}{}{CMe{:}C(COOEt)}{CMe{:}C(COOEt)}>CH_2,$$

crystallising with $\frac{1}{2}H_2O$ in yellow needles which melt at 52°, and lose water at 115°; by reduction with stannous chloride and ammonia, it yields another *base*, $C_{13}H_{19}NO_4$, which crystallises with $\frac{1}{2}H_2O$, and melts at 88°.

Ethylic lutidinedicarboxylate gives a nitroso-derivative, but has basic properties, and thus gives a *picrate*, $C_{13}H_{17}NO_4,C_6H_2(NO_2)_3{\cdot}OH$, which separates in long, yellow crystals melting at 118—119°; the original ethylic salt and its isomeride are found to have double the normal molecular weight by the boiling point method.

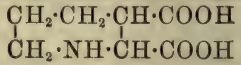
The authors conclude that the original ethylic dihydrolutidinedicarboxylate melting at 176—183° is wrongly named; it contains no pyridine nucleus, but is an open chain compound of the constitution $CH_2{:}C(COOEt){\cdot}CMe{:}N{\cdot}CMe{:}CH{\cdot}COOEt$. This compound, by the migration of one hydrogen atom, readily yields the closed chain imido-base, which is termed ethylic isodihydrolutidinedicarboxylate, and has the constitution $NH<\genfrac{}{}{0pt}{}{CMe{:}C(COOEt)}{CMe{:}C(COOEt)}>CH_2$. This compound is readily oxidised on exposure to air, yielding the labile form of ethylic lutidinedicarboxylate melting at 72°, to which the constitution $N\genfrac{}{}{0.4pt}{}{\diagup CMe{:}C(COOEt)\diagdown}{\diagdown CMe{:}C(COOEt)\diagup}CH$ must be assigned; this unstable form, on recrystallisation, then assumes the stable form which becomes electric on rubbing, and has the constitution



$$N<\genfrac{}{}{0pt}{}{CMe{\cdot}C(COOEt)}{CMe{:}C(COOEt)}>CH.$$

W. J. P.

**Dicarboxylic acids of the Piperidine Bases.** By WILHELM KOENIGS (*Ber.*, 1895, **28**, 3148—3150; compare the following abstract).—A number of the dicarboxylic acids of the piperidine bases have been synthetically prepared in order to throw light on the constitution of cincholeuponic acid, which is obtained by the oxidation of the quinine alkaloïds. In addition to those described in the succeeding abstract, the following compounds have been examined. The *hydrochloride of hexahydrocinchomeronic acid* melts and decomposes at 237°, whilst the *hydrochloride* of *hexahydrolepidinic acid* melts and decomposes at 222°. No attempt has yet been made to resolve these acids into optically active constituents. A. H.

**Reduction of Quinolinic acid.** By Emil Besthorn (*Ber.*, 1895, **28**, 3151—3160; compare the foregoing abstract).—When quinolinic acid, in dilute alcoholic solution, is reduced with sodium amalgam, it yields the lactone of δ-hydroxybutane-αγδ-tricarboxylic acid (Perlmutter, Abstr., 1893, i, 176); whilst, if it is dissolved in boiling amylic alcohol and treated with metallic sodium, it is converted into nipecotinic acid, carbonic anhydride being lost at the temperature of the experiment. On the other hand, again, reduction with metallic sodium and ethylic alcohol yields *hexahydroquinolinic acid*, 

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot COOH \\ | \qquad\qquad\qquad\quad | \\ CH_2\cdot NH\cdot CH\cdot COOH \end{array}$$

the product obtained is a mixture of two geometrically isomeric acids, which can be separated by means of their nitroso-compounds. Which of these acids is the *cis*-form, and which the *cis-trans*-form, has not yet been definitely decided. (1) One of the nitroso-acids is only sparingly soluble in cold water; it is, however, readily soluble in hot water, crystallises in large compact crystals, and melts and decomposes at 154°. The *barium salt* is very readily soluble in water, whilst the *silver* salt is only sparingly soluble. This nitroso-acid may be resolved into two optically active constituents by the fractional crystallisation of its strychnine salt. The new acids thus obtained, and the hexahydroquinolinic acids prepared from them, scarcely differ from the racemoïd forms, except in optical activity; they will shortly be more fully described. The *hydrochloride of hexahydroquinolinic acid*, obtained by the action of concentrated hydrochloric acid on the nitroso-acid, forms slender, white needles, melting and decomposing at 221°, whilst the *aurochloride* melts at 185°. The free acid separates from water in compact, white crystals melting at 253°; it is scarcely soluble in alcohol and other organic solvents. The *hydrochloride of methylic hexahydroquinolinate* melts and decomposes at 166—167°. (2) The more readily soluble nitrosohexahydroquinolinic acid was not itself isolated, but when decomposed with hydrochloric acid it yields the *hydrochloride of hexahydroquinolinic acid*, which melts at 239°, and, unlike the isomeric salt just described, is only sparingly soluble in concentrated hydrochloric acid. The *aurochloride* melts and decomposes at 195°. The free acid melts at 227°, and is much more readily soluble in water than its isomeride; it has hitherto only been obtained as a glassy mass. The hydrochloride melting at 239° is completely converted into the isomeric salt, melting at 221°, when it is dissolved in amylic alcohol, treated with sodium, isolated in the form of a nitroso-acid, and finally re-obtained from this compound by the action of hydrochloric acid. The *hydrochloride of methylic hexahydroquinolinate* melts and decomposes at 189—190°, whilst the corresponding *ethylic derivative* melts and decomposes at 204—205°.

Hexahydroquinolinic acid acts towards bases as a monobasic acid, whilst the nitroso-acid is dibasic.

It has so far proved impossible to resolve the acid melting at 227° into optically active constituents, although since the groups combined with its two asymmetric carbon atoms are dissimilar, it should, like the isomeride, be capable of such resolution. A. H.

**Optically Active 2-Pipecolines and "Isopipecoline."** By Wilhelm Marckwald (*Ber.*, 1896, **29**, 43—51).—Inactive synthetical 2-pipecoline can be separated into its active components by adding *d*-tartaric acid and concentrating, when *d*-2-pipecoline *d*-hydrogen tartrate crystallises out. From the mother liquor, the base is set free, and then made to crystallise with *l*-tartaric acid, when *l*-2-pipecoline *l*-hydrogen tartrate crystallises out. This process is repeated, *d*- and *l*-tartaric acid being used alternately to effect crystallisation; an almost quantitative separation can thus be effected. These two hydrogen tartrates both have the composition $C_6H_{13}N,C_4H_6O_6 + 2H_2O$; both melt at 65—66° or, when anhydrous, at 111—112°, and both form monoclinic crystals, which are enantiomorphous but otherwise identical; $a : b : c = 1{\cdot}1698 : 1 : 1{\cdot}7477$; $\beta = 81° 20'$. The hydrochlorides, cadmioiodides, platinochlorides, aurochlorides, picrates, and dithiocarbamates, ($C_6H_{12}N{\cdot}CS{\cdot}SH{\cdot}C_6H_{13}N$), melt respectively at 190° (205°), 147° (131°), 194° (186°), 131—132° (118—119°), 116—117° (127—128°), 141—142° (126°); the numbers given in brackets are the melting points of the corresponding salts of inactive 2-pipecoline. *l*-2-Pipecoline, liberated from its *l*-hydrogen tartrate prepared as above, has a rotation $\alpha_D = -32{\cdot}0°$, in a tube 100 mm. long, and is of the same magnitude as that of the *d*-isomeride; it had not hitherto been obtained pure.

*d*-2-Pipecoline *l*-hydrogen tartrate and *l*-2-pipecoline *d*-hydrogen tartrate both crystallise with $H_2O$; both melt at 45—46°, and when anhydrous at 126°.

2-Pipecoline hydrogen racemate can be prepared from inactive 2-pipecoline and racemic acid, or from *d*-2-pipecoline *d*-hydrogen tartrate and *l*-2-pipecoline *l*-hydrogen tartrate, or from *d*-2-pipecoline *l*-hydrogen tartrate and *l*-2-pipecoline *d*-hydrogen tartrate. It crystallises with $H_2O$ in monoclinic crystals; $a : b : c = 2{\cdot}670 : 1 : 1{\cdot}368$; $\beta = 85° 46{\cdot}5'$; and melts at 85°.

Ladenburg's statement (Abstr., 1894, 306) that a new substance, isopipecoline, is obtained when *d*-2-pipecoline hydrochloride is distilled with zinc dust, is incorrect; what really happens is a partial conversion of *d*- into *l*-pipecoline. If *l*-pipecoline chloride is boiled in an atmosphere of hydrogen, it undergoes a partial conversion into the *d*-isomeride. C. F. B.

**α-Naphthylpiperidine.** By Julius Abel (*Ber.*, 1895, **28**, 3106—3111; compare Abstr., 1890, 1002).—α-Naphthylpiperidine (*loc. cit.*)

is formed when piperidine (8·5 grams) is heated with α-naphthol (14·4 grams) at 250—260° for 4—5 hours; it is a pale yellow oil which boils at 215° under a pressure of 35 mm., and exhibits a beautiful blue fluorescence. The hydrochloride forms colourless crystals melting at 178—179°; the *aurochloride* melts at 128—129°, and the *picrate* crystallises in yellow needles, and melts at 179—180°; the *ferrocyanide* separates in colourless crystals, and the *mercurichloride* is amorphous.

*Tetrahydro-α-naphthylpiperidine* is obtained by adding a solution of α-naphthylpiperidine (15 grams) in dry amylic alcohol (200 grams) to molten sodium (25 grams); it is a pale, yellow oil which boils at 218° under a pressure of 63 mm., and reduces cold, alcoholic silver nitrate. The *hydrochloride* crystallises with difficulty, and the *mercurichloride* is amorphous, the *ferrocyanide* being obtained in white crystals; the *platinochloride* forms small, lustrous crystals, melting at 190—192°, and the *aurochloride* crystallises in golden-yellow leaflets, and melts at 148—149°. Oxidation of tetrahydro-α-naphthylpiperidine with potassium permanganate in presence of alkali gives rise to adipic acid. M. O. F.

**2 : 3- and 3 : 4-Dibromoquinoline.** By ADOLPH CLAUS [and, in part, KARL LODHOLZ and FRITZ HIRSCHBRUNN] (*J. pr. Chem.*, 1896, [2], **53**, 25—38).—2 : 3-Dibromoquinoline melts at 68°, and 3 : 4-dibromoquinoline at 135°, not 95° and 124° respectively as previously stated (Abstr., 1890, 172).

3 : 4-Dibromoquinoline *platinochloride* and *methiodide* are described.

The bromination of 3 : 4-dibromoquinoline hydrobromide in chloroform solution produces 3 : 4 : 3′-*tribromoquinoline*, which melts at 149°, and was formerly described as 3 : 4 : 4′-tribromoquinoline (Abstr., 1894, i, 473); the *platinochloride* is described.

3 : 4 : 1-*Dibromonitroquinoline* is the sole product of the nitration of 3 : 4-dibromoquinoline in the usual manner; it sublimes in the form of lustrous needles and melts at 152°: its basic properties are very feeble; the *platinochloride* is described.

2 : 3-Dibromoquinoline differs from the 3 : 4-derivative in its volatility in steam at atmospheric pressure; its *platinochloride* and *methiodide* are described.

2 : 3 : 1-*Dibromonitroquinoline* is the more abundant product when 2 : 3-dibromoquinoline is nitrated without warming; it sublimes in nearly colourless, lustrous crystals, melts at 191°, and dissolves freely in ether and chloroform, but only sparingly in alcohol, and not at all in water; the *platinochloride* is described, but no methiodide could be obtained. The corresponding *amido*-derivative crystallises in colourless, slender needles, and melts at 68°.

1 : 2 : 3-*Tribromoquinoline* is prepared from 2 : 3 : 1-dibromamidoquinoline through the diazo-reaction; it crystallises in colourless needles, melts at 84°, and does not easily sublime; the *hydrochloride* and *platinochloride* are described.

2 : 3 : 4-*Dibromonitroquinoline* is the more abundant product of the nitration of 2 : 3-dibromoquinoline when the temperature is raised; it is more soluble in alcohol than is the accompanying 2 : 3 : 1-derivative,

and crystallises and sublimes in colourless needles melting at 165°. The *methiodide* is easily prepared (compare the 2 : 3 : 1-derivative), and melts and decomposes at about 250—252°. The *platinochloride* is described. The corresponding *amido*-derivative crystallises in small, colourless needles, and melts at 119°.

2 : 3 : 4-*Tribromoquinoline*, prepared like the 1 : 2 : 3-derivative, crystallises and sublimes in colourless needles, and melts at 124°.

2 : 3 : 3′-*Tribromoquinoline* is prepared by the Claus-Collischonn method (bromination of the appropriate dibromoquinoline hydrobromide in chloroform solution) from 2 : 3-dibromoquinoline; it sublimes in lustrous, colourless prisms, and melts at 116·5°. The *platinochloride* and the *methiodide* are described. A. G. B.

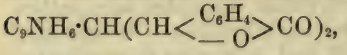
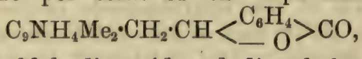
**Action of Bromine on Para- and Ortho-Hydroxyquinoline.** By Adolph Claus and Hans Howitz (*J. pr. Chem.*, 1895, [2], **52**, 532—547).—The authors have previously stated that the red dibromide obtained by adding bromine (2 atoms) to 4 : 3-bromhydroxyquinoline hydrobromide suspended in chloroform decomposes when exposed to air, with loss of hydrogen bromide and formation of a dibromo-3-hydroxyquinoline. This statement is incorrect; the compound merely loses the two atoms of bromine, the original 4 : 3-bromohydroxyquinoline being left.

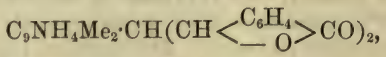
1 (? 2) : 4 : 3′ : 3-*Tribromhydroxyquinoline* is obtained when the foregoing dibromide, or a mixture of 4 : 3-bromohydroxyquinoline with bromine (2 mols.) is heated in a sealed tube at 200—250°. It crystallises in slender, silky, colourless needles, melts at 257°, and dissolves very sparingly in mineral acids and in alcohol, but freely in warm glacial acetic acid. Oxidation by potassium permanganate converts it into 3-bromopyridinedicarboxylic acid and 3-bromonicotinic acid; this settles, to some extent, its orientation.

2 : 4 : 1-*Dibromohydroxyquinoline hydrobromide* separates as a yellow crystalline precipitate when bromo-1-hydroxyquinoline is brominated in chloroform solution; it melts at 250°, and sublimes slowly in the form of slender needles; when warmed with water, it yields the corresponding *base*, which separates in crystalline flocks, and melts at 196°. When this dibromhydroxyquinoline is brominated in chloroform, the *dibromide* of the hydrobromide is precipitated in yellow needles or prisms, which melt at 160—170°, the molten mass rapidly losing bromine; in water, this compound loses hydrogen bromide without loss of its bromine. By heating the dibromide in a sealed tube at 250°, 2 : 4 : 3′ : 1-*tribromhydroxyquinoline* may be obtained; it is at first a yellow powder, but sublimes in colourless needles, which melt at 169—170°; oxidation with permanganate converts it into 3-bromopyridinedicarboxylic acid. The authors regard this tribromhydroxyquinoline as identical with that obtained by Claus and Heermann by the action of phosphorus pentabromide on 1 : 4-hydroxyquinolinesulphonic acid (Abstr., 1891, 82). A. G. B.

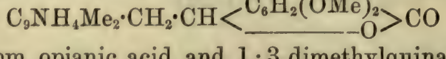
**3-Ethoxyquinoline.** By C. Grimaux (*Compt. rend.*, 1895, **121**, 749—751).—3-*Ethoxyquinoline* or *quinethoïl*, $C_9NH_6{\cdot}OEt$, is an oily liquid obtained by the action of glycerol and sulphuric acid on ethyl phenyl ether. It boils at 290—292° without decomposing, and with inorganic acids forms crystalline salts, the solutions of which show fluorescence similar to that of quinine. The nitrate crystallises in needles melting at 165°. The salts with organic acids are decomposed by water. The *nitro*-derivative is not obtained by the action of nitric acid alone, but is prepared by adding nitric acid to a solution of the base in sulphuric acid, and treating the product (the nitrate of the nitro-derivative) with potassium or sodium hydroxide, or by adding the nitrate of the base to sulphuric acid, diluting with water, and precipitating with ammonia. It melts at 110°, crystallises in needles or in flat rhomboïdal prisms according to the conditions, and has feebly basic properties. The *amido*-derivative crystallises from boiling water in sulphur-yellow prisms containing 1 mol. $H_2O$, and, when anhydrous, melts at 110°. With acids, it forms red monacid salts, which dye silk a pale yellow; the diacid salts are colourless. The diazo-derivative yields coloured compounds.

3-Ethoxyquinoline is without any effect even in the simplest intermittent fevers, and has no antipyretic properties. C. H. B.

**Action of Orthoaldehydic acids on Quinaldine in Presence of Zinc Chloride.** By K. Nencki (*Ber.*, 1896, 29, 187—190; compare M. Nencki (Abstr., 1894, i, 518).—*Phthalidylquinaldine*, $C_9NH_6\cdot CH_2\cdot CH<{C_6H_4 \atop O}>CO$, is prepared by heating aqueous solution of phthaldehydic acid and quinaldine, in molecular proportion, with zinc chloride during eight hours; the product is extracted with dilute hydrochloric acid, and the solution treated with soda; the precipitate crystallises from alcohol in colourless needles, and melts at 104°. The *platinochloride*, $(C_{18}H_{13}O_2N)_2,H_2PtCl_6$, is yellow and crystalline; the *aurochloride* has also been prepared. *Diphthalidylquinaldine*,  $C_9NH_6\cdot CH(CH<{C_6H_4 \atop O}>CO)_2$, is obtained, along with the preceding compound, and can be separated from it by means of its insolubility in hydrochloric acid; it crystallises from absolute alcohol in needles, and melts at 192°. The combined yield is 50 per cent. of the theoretical, including 10 per cent. of the diphthalidyl. *Phthalidyldimethylquinaldine*,  $C_9NH_4Me_2\cdot CH_2\cdot CH<{C_6H_4 \atop O}>CO$, $[Me_2 = 1:3]$, prepared from phthaldehydic acid and dimethylquinaldine, crystallises in colourless needles, melts at 116°, and is insoluble in dilute alkali. *Diphthalidyldimethylquinaldine*,

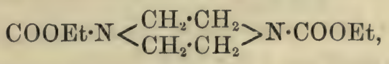


$$C_9NH_4Me_2\cdot CH(CH<{C_6H_4 \atop O}>CO)_2,$$

is colourless, crystalline, melts at 224°, and is formed in small quantity together with the preceding compound. *Opianyldimethylquinaldine*,  $C_9NH_4Me_2\cdot CH_2\cdot CH<{C_6H_2(OMe)_2 \atop O}>CO$ $[Me_2 = 1:3]$, prepared from opianic acid and 1:3-dimethylquinaldine, crystallises in colourless, slender needles, melts at 132°, and dissolves in alkali

(30 per cent.) only after prolonged boiling. The *platinochloride*, $(C_{28}H_{21}O_4N)_2,H_2PtCl_6$, forms yellow crystals. The formulæ given to the above compounds accord with their insolubility in alkali, and in their formation the aldehydic acids react as hydroxyphthalides (compare Liebermann, this vol., i, 232). J. B. T.

**Derivatives of Piperazine.** By G. Rosdalsky (*J. pr. Chem.*, 1896, [2], **53**, 19—24).—*Ethylic piperazine*-1 : 4-*dicarboxylate*,



$$\mathrm{COOEt{\cdot}N}<\substack{\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}}>\mathrm{N{\cdot}COOEt},$$

is prepared by shaking an aqueous solution of piperazine with ethylic chlorocarbonate and potash, and extracting with ether; it crystallises in needles, melts at 42°, boils at 315°, and dissolves in the usual solvents.

*Piperazine*-1 : 4-*dicarboxylamide*, $C_4N_2H_8(CONH_2)_2$, is precipitated when cold concentrated solutions of piperazine hydrochloride and potassium cyanate are mixed; it crystallises from hot water in lustrous, rhombic crystals, and from boiling alcohol in short prisms; it is insoluble in ether and benzene. The corresponding *anilide*, $C_4N_2H_8(CO{\cdot}NHPh)_2$, is an amorphous, insoluble substance, precipitated by adding phenylic isocyanate to an aqueous solution of piperazine.

*Tri-carbonylpiperazine*, $(C_4N_2H_8{:}CO)_3$, separates as an amorphous precipitate when carbonyl chloride is passed into an alkaline solution of piperazine; it is insoluble in the usual solvents.

*Tri-phthalylpiperazine*, $(C_4N_2H_8<\substack{CO\\ CO}>C_6H_4)_3$, is an amorphous precipitate, formed when phthalic chloride is added to an alkaline solution of piperazine.

*Piperazine*-1 : 4-*diphenylsulphone*, $C_4N_2H_8(SO_2Ph)_2$, from benzene sulphonic chloride and piperazine, is an amorphous precipitate.

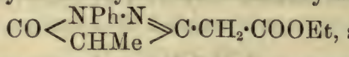
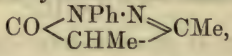
1 : 4-*Methylenepiperazine*, $C_4N_2H_8{:}CH_2$, from piperazine and formaldehyde, is a white precipitate, insoluble in water, alcohol, ether, benzene, and caustic soda, and decomposed by dilute acids into the parent substances.

*Piperazine ethylic oxalate*, $C_4N_2H_{10},(COOH{\cdot}COOEt)_2$, is obtained by heating hydrated piperazine with ethylic oxalate in alcoholic solution; it crystallises from water in thick prisms, and melts at 181°. Alcoholic ammonia converts this compound into *piperazine oxamate*, $C_4N_2H_{10},(COOH{\cdot}CONH_2)_2$, which crystallises in monoclinic tables.

1 : 4-*Diethoxalylpiperazine*, $C_4N_2H_8(CO{\cdot}COOEt)_2$, is obtained when anhydrous piperazine and ethylic oxalate are heated together in absolute alcohol; it is separated from other products by boiling benzene, and melts at 115° (compare Schmidt and Wichmann, Abstr., 1892, 210).

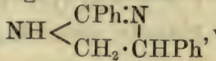
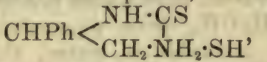
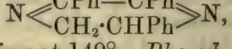
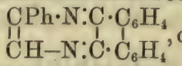
The *compound*, $C_{16}H_{26}N_2O_4$, is formed when ethylic acetoacetate and piperazine are warmed together; it crystallises in white, felted needles, melts at 140°, and dissolves sparingly in ether and benzene, but not in water.

Carbonic anhydride produces a crystalline precipitate, $C_5H_{10}N_2O_2$, in an alcoholic solution of piperazine. A. G. B.

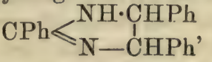
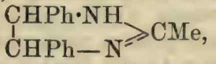
**Steric Hindrances to Chemical Reactions.** By Pavel Iw. Petrenko-Kritschenko (*Ber.*, 1895, **28**, 3203—3207; compare this vol., i, 134). The ethereal salt, formed by the action of phenylhydrazine on ethylic methylacetonedicarboxylate, is shown to have the constitution,  $CO<\begin{array}{l}NPh\cdot N\\CHMe\end{array}>C\cdot CH_2\cdot COOEt$, since the acid formed on hydrolysis loses carbonic anhydride when heated, and yields Knorr's dimethylphenylpyrazolone,  $CO<\begin{array}{l}NPh\cdot N\\CHMe-\end{array}>CMe$, on distillation in a vacuum.

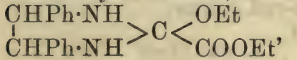
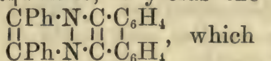
The author criticises some of the conclusions drawn by V. Meyer (this vol., i, 145) from his work on the etherification of triphenylacetic and triphenylacrylic acids. In contradistinction to V. Meyer, the author regards the phenyl-group as equivalent to a primary, rather than to a tertiary, radicle. This conclusion is supported by reference to the author's own work, and also to that of Meyer and of Lean.

Victor Meyer, in an appended note, states that he does not agree with all the author's conclusions. J. J. S.

**Aromatic Homologues of Ethylenediamine.** By Franz Feist and Hugo Arnstein (*Ber.*, 1895, **28**, 3167—3181; compare Abstr., 1895, i, 274).—The dibenzoyl compound of phenylethylenediamine, when heated in a current of hydrogen chloride at 240°, is converted into 2 : 4-*diphenyldihydroglyoxaline*,  $NH<\begin{array}{l}CPh{:}N\\CH_2\cdot CHPh\end{array}$, which crystallises in hard, colourless prisms, melting at 78°. *Diacetophenylethylenediamine* crystallises in snow-white plates, melting at 152°. The *thiocarbamate of the base*,  $CHPh<\begin{array}{l}NH\cdot CS\\CH_2\cdot NH_2\cdot SH\end{array}$, melts and decomposes at 97°. *Phenylethylenethiocarbamide* crystallises in white plates, and melts at 184°. The diamine does not yield a well characterised product with ethylic oxalate or benzaldehyde, but readily reacts with benzile, forming 2 : 3 : 5-*triphenyl*-5 : 6-*dihydropyrazine*,  $N<\begin{array}{l}CPh—CPh\\CH_2\cdot CHPh\end{array}>N$, which crystallises in bronze-coloured plates, melting at 149°. *Phenylphenanthrapyrazine*,  $\begin{array}{l}CPh\cdot N{:}C\cdot C_6H_4\\CH—N{:}C\cdot C_6H_4\end{array}$, crystallises in silky, yellow needles, melting at 190°. *Phenyl-β-naphthapyrazine* melts at 187°.

Diphenylethylenediamine forms a *bitartrate*, which crystallises in fascicular groups of needles, melting with decomposition at 165—166°. The fractional crystallisation of this salt from warm water resulted in the separation of its two optically active components, the dextrorotatory base forming the more readily soluble salt. The two components have not yet been completely separated. An attempt to convert the racemic form of the base into hydrobenzoïn by means of the action of sodium nitrite, resulted in the production of a very small amount of isohydrobenzoïn, which must therefore be the racemic form of this compound. Small amounts of isodiphenylhydroxyethylamine and of diphenylacetaldehyde were also obtained in the same reaction.

*Diacetophenylethylenediamine* is a white powder, which melts above 360°. The *dibenzoyl-compound* melts at 287°. *Trinitrodibenzodiphenylethylenediamine* may be obtained by direct nitration, and forms a yellow powder, melting at 137° with decomposition. The dibenzoyl-compound is remarkably stable, and can only be converted into an anhydro-base by hydrogen chloride at 260°. 2 : 4 : 5-*Triphenyl*-4 : 5-*dihydroglyoxaline*,  $\mathrm{CPh}{<}\begin{array}{l}\mathrm{NH\cdot CHPh}\\ \mathrm{N{-}CHPh}\end{array}$, prepared as just described, is isomeric with amarine, and melts at 175°. 2 : 4 : 5-*Methyldiphenyl*-4 : 5-*dihydroglyoxaline*,  $\begin{array}{l}\mathrm{CHPh\cdot NH}\\ \mathrm{CHPh{-}N}\end{array}{>}\mathrm{CMe}$, may be prepared in a similar manner, and melts at 162°. *Diphenylethylenedicarbamide* crystallises in colourless needles, and melts above 360°. The *dithiocarbamide* melts and decomposes at 192°. *Diphenylethylenediamine thiocarbamate* is a light yellow, crystalline powder, which melts at 132°. *Diphenylethylenethiocarbamide* is obtained by the distillation of the foregoing compound, and is a white, granular powder, melting at 183—184°.

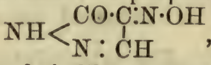
The base unites with two molecular proportions of ethylic oxalate, forming an additive compound, which melts at 164°. When heated with ethylic oxalate, on the other hand, a compound of the formula,  $\begin{array}{l}\mathrm{CHPh\cdot NH}\\ \mathrm{CHPh\cdot NH}\end{array}{>}\mathrm{C}{<}\begin{array}{l}\mathrm{OEt}\\ \mathrm{COOEt}\end{array}$, is obtained in white crystals, melting and decomposing at 242°. The *dibenzylidene derivative* of the base melts at 152°. Diphenylethylenediamine reacts with benzil to form tetraphenylpyrazine. With phenanthraquinone, it yields the compound, 2 : 3-*diphenylphenanthrapyrazine*,  $\begin{array}{l}\mathrm{CPh\cdot N\cdot C\cdot C_6H_4}\\ \mathrm{CPh\cdot N\cdot C\cdot C_6H_4}\end{array}$, which crystallises in slender, light-brown needles, melting at 265°. A. H.

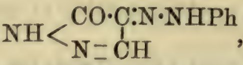
**Pyrazolone.** By Ludwig Knorr (*Ber.*, 1896, **29**, 249—259; compare von Rothenberg, Abstr., 1893, i, 180, 367, 428, 611, and 729; 1894, i, 349, 350, and 622; 1895, i, 302, 571, and 686; Ruhemann, Abstr., 1894, i, 476).—The author points out that the pyrazolone described by Ruhemann has properties entirely different from those of the pyrazolone described by von Rothenberg, and as the possibility of isomerism is theoretically impossible, one of the statements must be wrong. The two formulæ given by Ruhemann for pyrazolone and isopyrazolone, the author considers, represent desmotropic forms of the same substance. The author has prepared pyrazolone from hydrazine hydrate and ethylic formylacetate, and finds that it agrees in all its properties with the substance described by Ruhemann, and he therefore concludes that the oily substance (b. p. 156—157°) described by von Rothenberg can only be a solution of pyrazolone, and not the pure substance, especially as it shows no analogy in its general properties to 1 : 3-phenylmethyl-5-pyrazolone and 3-methyl-5-pyrazolone, which have been previously prepared.

Pyrazolone, as obtained by the action of hydrazine sulphate on the sodium salt of ethylic formylacetate in the presence of free alkali, crystallises from toluene or xylene in minute needles, begins to sinter at 160°, and melts at 163—164°; it has no odour, is readily soluble in water and alcohol, but only sparingly in ether. It has reducing properties, is coloured reddish-brown by ferric chloride, and is only slightly volatile with steam. When heated, it sublimes, at the same time undergoing decomposition. It is further characterised by possessing both acid and basic properties; solutions of pyrazolone cannot be titrated with litmus as an indicator, since the litmus is turned blue when only about 3/10ths of the theoretical quantity of alkali has been added. An oily and extremely hygroscopic *hydrochloride* may be obtained, but it gives no precipitates with either platinum or gold chloride. In contradistinction to von Rothenberg's compound, it is not decomposed when heated with concentrated hydrochloric acid at 100°.

The sodium salt may be obtained as a solid, hygroscopic residue on evaporating a solution of pyrazolone in the requisite quantity of sodium hydroxide solution. The solution of the sodium salt yields precipitates with silver nitrate, barium chloride, cobalt sulphate, nickel sulphate, copper sulphate, and mercuric chloride solutions.

4-*Benzylidenepyrazolone*, $C_3N_2H_2O{:}CHPh$, crystallises in minute, orange coloured needles, and melts at 200°; whereas Rothenberg describes it as a semi-solid mass of a purple-red colour.

4-*Isonitrosopyrazolone*,  $\mathrm{NH}<\begin{array}{l}\mathrm{CO\cdot C{:}N\cdot OH}\\ \mathrm{N:CH}\end{array}$, crystallises from its aqueous solutions in long, hair-like needles, or in small, compact, yellow prisms; it melts at 180—181°, and, at the same time, undergoes decomposition. According to von Rothenberg, it crystallises in brown needles and melts at 87°. The *silver salt* forms deep red, felted needles.

The *hydrazone*,  $\mathrm{NH}<\begin{array}{l}\mathrm{CO\cdot C{:}N\cdot NHPh}\\ \mathrm{N=CH}\end{array}$, crystallises in orange coloured plates, and melts at 196° (Rothenberg gives 185°). The *paratolylhydrazone* melts and decomposes at 223° (Rothenberg, 219°). The author thinks that his compounds are identical with those described by von Rothenberg, but that the latter were by no means pure. Pyrazolone, prepared by Ruhemann's method (Trans., 1895, 1008), gives derivatives identical with those described above. J. J. S.

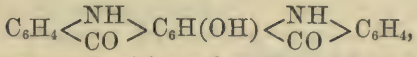
**Metallic Double Salts of Antipyrine (Dimethylphenylpyrazolone).** By LEOPOLD VAN ITALLIE (*Ned. Tydschr. Pharm.*, 1895, 7, 295—298).—*Antipyrine zinc chloride*, $(C_{11}H_{12}N_2O)_2,ZnCl_2$.—If aqueous solutions of zinc chloride and antipyrine are mixed in molecular proportion, oily globules are formed, which first become pasty and afterwards crystalline. The crystals are anhydrous, and melt at 155°. The salt is also obtained by slowly evaporating a mixture of zinc chloride and antipyrine in alcoholic solution, or by mixing this solution with ether.

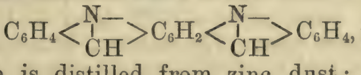
The corresponding iodide forms well-defined crystals, showing double refraction, and the bromide colourless crystals, moderately soluble in water.

On adding a solution of mercurous nitrate to an alcoholic solution of antipyrine, a greyish-black deposit is obtained, consisting of a compound of antipyrine with both mercurous and mercuric nitrates, The amount of combined mercury is, however, very variable, and there is always a small quantity of metallic mercury in the precipitate.

L. DE K.

**Quinacridine.** By STEFAN NIEMENTOWSKI (*Ber.*, 1896, **29**, 76—83).—The condensation of phloroglucinol with anthranilic acid yields a derivative of quinacridine, the name given by the author to a base, the structure of which resembles that of anthracene or phenanthrene.

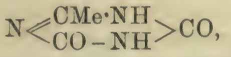
*Hydroxyquinacridone*,  $C_6H_4<\genfrac{}{}{0pt}{}{NH}{CO}>C_6H(OH)<\genfrac{}{}{0pt}{}{NH}{CO}>C_6H_4$, is obtained by heating phloroglucinol with anthranilic acid at 150° for 15—20 minutes, and then at 200—230° for 1—2 hours; it remains solid at 370°, becoming black at 410°. This substance is insoluble in the usual organic solvents, but crystallises in minute cubes from phenol and phenylhydrazine; the solution in concentrated sulphuric acid is yellow, and exhibits green fluorescence. The *acetoxyquinacridone* is amorphous, and undergoes no change at 360°. The *trinitro* derivative is insoluble in organic solvents and dissolves in alkalis; it decomposes and becomes black at 270—280°.

*Quinacridine*,  $C_6H_4<\begin{smallmatrix}N—\\ |\\ CH\end{smallmatrix}>C_6H_2<\begin{smallmatrix}N—\\ |\\ CH\end{smallmatrix}>C_6H_4$, is formed when hydroxyquinacridone is distilled from zinc dust; it crystallises from benzene in colourless leaflets, and melts at 221°. A *compound*, which is probably an isomeride, is also formed, crystallising from the mother liquor and melting at 213°; it forms a platinochloride, resembling that of acridine, and this base is also produced when hydroxyacridone is submitted to the treatment indicated.

*Tetrahydroquinacridine*, $C_{20}H_{16}N_2$, is obtained by reducing quinacridine in alcoholic solution with sodium amalgam; it crystallises from benzene in golden-yellow leaflets, and melts at 272°, softening at 255°. Acetic anhydride dissolves it with the production of an intense blood-red solution, which deposits quinacridine on cooling; the solution in boiling benzene is yellow, and exhibits a beautiful, green fluorescence.

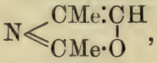
M. O. F.

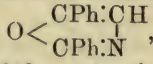
**Methyldioxytriazine (Acetoguanamide).** By A. OSTROGOVICH (*Annalen*, 1895, **288**, 318—321).—*Methyldioxytriazine*,



$$N<\genfrac{}{}{0pt}{}{CMe\cdot NH}{CO-NH}>CO,$$

identical with acetoguanamide, described by Nencki (*Ber.*, 1876, **9**, 234), is obtained by heating acetylurethane (6 grams) with carbamide (2·7 grams) for six hours at 140—150°, ethylic acetate being formed at the same time. The *hydrochloride* crystallises in needles, and the *platinochloride* is yellow; the *silver* derivative is white, and the *lead* derivative is crystalline. Dilute nitric acid converts methyldioxytriazine into cyanuric acid, and bromine gives rise to a *tribromo*-derivative, which yields cyanuric acid and bromoform when treated with boiling water. M. O. F.

$\alpha:\mu$-**Dimethyloxazole.** By ADOLF SCHUFTAN (*Ber.*, 1895, **28**, 3070—3071).—This substance,  $\mathrm{N}{<}\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CMe{\cdot}O}\end{matrix}$, can be obtained from chloracetone and acetamide, contrary to Lewy's statement (Abstr., 1888, 1101), by heating them in the proportions of $1\frac{1}{2}:1$ parts by weight for eight hours at 110—120°; much of the acetamide remains unchanged, however. It is a colourless liquid, with an odour like that of pyridine and hardly distinguishable from that of $\alpha:\mu$-dimethylthiazole; it boils at 108°; its *hydrochloride*, *platinochloride* (decomposing at 196°), *aurochloride*, and *mercurochloride* (melting between 82—90°) were prepared. C. F. B.

**New Synthesis of Oxazoles.** By EMIL FISCHER (*Ber.*, 1896, **29**, 205—214).—When hydrogen chloride is passed into a cooled ethereal solution of benzaldehydecyanhydrin and benzaldehyde, the *hydrochloride* of *$\beta:\mu$-diphenyloxazole*,  $\mathrm{O}{<}\begin{matrix}\mathrm{CPh{:}CH}\\ \mathrm{CPh{:}N}\end{matrix}$, crystallises out. This melts and decomposes at 160—165°; water decomposes it, precipitating the oxazole, which melts at 74° and boils just above 360°; the *methiodide* melts and decomposes at 196° (corr. 201°), and has the character of a quaternary base. The oxazole, in acetic acid solution, is oxidised by chromic acid to *phenylglyoxyl-benzamide*,

$$\mathrm{CPhO{\cdot}NH{\cdot}CO{\cdot}CPhO},$$

which melts at 142—143° (corr. 146°). When reduced with sodium in boiling alcoholic solution, the oxazole yields *benzylphenylhydroxyethylamine*, $\mathrm{CH_2Ph{\cdot}NH{\cdot}CH_2{\cdot}CHPh{\cdot}OH}$, which melts at 100—101° (corr. 104°), and distils without decomposing. The *hydrochloride* of this base melts at 220° (corr. 226°); the *nitrosamine* melts at 93° (corr. 95°), and does not give Liebermann's reaction. The base is reduced by hydriodic acid at 140—150° to *benzylphenylethylamine*, $\mathrm{CH_2Ph{\cdot}NH{\cdot}CH_2{\cdot}CH_2Ph}$, which boils at 327—328° under 750 mm. pressure; the *hydriodide* melts at 227° (corr. 233°), the *hydrochloride* at 264—266°, and the *sulphate* at 186—187° (corr. 191—192°). This base is more conveniently prepared by reducing with sodium in boiling alcoholic solution the condensation product of benzylamine with phenylacetaldehyde.

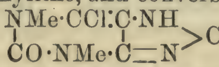
$\beta:\mu$-Diphenyloxazole can also be prepared by warming benzamide with crude phenylbromacetaldehyde, $\mathrm{CHPhBr{\cdot}CHO}$. This last is itself obtained by brominating a cooled chloroform solution of phenylacetaldehyde, and distilling off the chloroform in a vacuum; the product can be distilled under 1 mm. pressure.

The cyanhydrins of aliphatic aldehydes do not yield oxazoles in the manner described above. Acetaldehyde cyanhydrin and benzaldehyde, if left in ethereal solution containing 2 per cent. of hydrogen chloride, condense to *benzylidenelactamide*,

$$OH{\cdot}CHMe{\cdot}CO{\cdot}N{:}CHPh,$$

which melts at 130—131° (corr. 133—134°). C. F. B.

**Synthesis of Caffeïne.** By Emil Fischer and Lorenz Ach (*Ber.*, 1895, **28**, 3135—3143; compare this vol., i, 12).—The synthesis of caffeïne is effected by means of the following operations: (1) Production of dimethylbarbituric acid from malonic acid and dimethylcarbamide; (2) conversion of dimethylbarbituric acid into dimethylvioluric acid under the influence of nitrous acid; (3) reduction of dimethylvioluric acid to dimethyluramil, and transformation of the latter into dimethylpseudouric acid by means of potassium cyanate; (4) conversion of dimethylpseudouric acid into $\gamma$-dimethyluric acid (*loc. cit.*); (5) formation of chlorotheophylline by the action of phosphorus pentachloride on $\gamma$-dimethyluric acid; (6) reduction of chlorotheophylline to theophylline, and conversion of the latter into caffeïne.

*Chlorotheophylline*,  $\begin{array}{l}NMe{\cdot}CCl{:}C{\cdot}NH\\ |\qquad\qquad\;\; |\\ CO{\cdot}NMe{\cdot}C{=\!=}N\end{array}\!\!>CO$, is obtained by heating an intimate mixture of $\gamma$-dimethyluric acid, phosphorus pentachloride (2 parts) and phosphorus oxychloride (4 parts) in sealed tubes at 150° for $2\frac{1}{2}$ hours; it crystallises from acetone in aggregates of colourless needles, which melt and decompose about 300°. It is very sparingly soluble in chloroform, but dissolves more freely in acetone, and is readily soluble in hot alcohol; it dissolves in 150 parts of boiling water, forming an acid solution, and is readily soluble in ammonia, alkalis, and concentrated mineral acids. Chlorine water produces the change characteristic of xanthine and its derivatives. The *sodium* and *silver* derivatives crystallise in slender, white needles, the latter substance being insoluble in water, and gradually becoming dark when exposed to light. When chlorotheophylline is reduced with hydriodic acid, theophylline is produced (Kossel, Abstr., 1888, 1114); the action of methylic iodide on the silver derivative gives rise to chlorocaffeïne.

*Bromotheophylline* is formed when a mixture of phosphorus pentabromide and phosphorus oxychloride acts on $\gamma$-dimethyluric acid, chlorotheophylline being produced at the same time; it is also obtained by heating theophylline with bromine for four hours at 100° and subsequently at 150°. Bromotheophylline separates from alcohol in colourless crystals, and melts and decomposes at 315—320° (uncorr.); it is very sparingly soluble in hot water, but dissolves readily in ammonia and alkalis. Hydriodic acid readily converts it into theophylline.

Dimethylbarbituric acid is converted into the sodium derivative of dimethylvioluric acid by adding a concentrated solution of sodium nitrite to an aqueous solution of the acid at 60°; the sodium derivative contains $3H_2O$ (compare Andreasch, Abstr., 1895, i, 337), which is removed at 115°. Anhydrous dimethylvioluric acid melts at 141°, and in the hydrated condition at 124° (compare *loc. cit.*, and Techow, Abstr., 1895, i, 84). M. O. F.

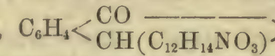
**Morphine.** By E. VONGERICHTEN (*Ber.*, 1896, **29**, 65—68).—The author considers that there is much evidence to show that morphine must have the nitrogen atom attached directly to a carbon atom of the benzene ring. He explains the decomposition of methylmorphimethine methohydroxide, when its aqueous solution is evaporated, by the equation $C_{18}H_{20}MeNO_3,Me{\cdot}OH = NMe_3 + C_{15}H_{10}O_2 + C_2H_4 + 2H_2O$. The compound $C_{15}H_{10}O_2$ is a phenanthrene derivative, and it yields a *tetrabromo-derivative*, $C_{15}H_6Br_4O_2$, which melts at 290°.

C. F. B.

**Synthesis of an Isomeric Narcotine.** By CARL T. LIEBERMANN (*Ber.*, 1896, **29**, 183—187).—Opianic acid and hydrocotarnine are mixed in molecular proportion and introduced into sulphuric acid (about 73 per cent.) free from nitrites, the liquid is well cooled, and after 12 hours diluted with ice-cold water, the unaltered opianic acid is removed, and on the addition of soda *isonarcotine*, $C_{22}H_{23}NO_7$, is precipitated; it crystallises from alcohol in colourless needles or prisms, melts at 194°, and is insoluble in alkalis. With pure concentrated sulphuric acid, a carmine coloration is obtained, the production of which may also be used as a test for the presence of opianic acid, cotarnine, or hydrocotarnine. The yield is excellent. When boiled with baryta water, the *salt*,

$$[C_{12}H_{14}NO_3{\cdot}CH(OH){\cdot}C_6H_2(OMe)_2{\cdot}COO]_2Ba,$$

is formed, from which isonarcotine is regenerated by successive treatment with sulphuric acid and soda. The *hydrochloride*, $C_{22}H_{23}NO_7,HCl + 2H_2O$, is crystalline, readily soluble, and without physiological action on rabbits. The *hydrobromide* is more sparingly soluble than the hydrochloride; the *hydriodide* is practically insoluble in cold water, and, like the *nitrate*, crystallises in colourless needles. The *platinochloride* and *aurochloride* are yellow. Attempts to synthesise narcotine from meconine and cotarnine, or hydrastine from meconine and hydrastinine, and from opianic acid and hydrohydrastinine have hitherto been unsuccessful.

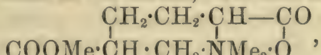
*Hydrocotarninephthalide*, 
$C_6H_4{<}\begin{matrix}CO\text{———}\\CH(C_{12}H_{14}NO_3)\end{matrix}{>}O$, is prepared, in a similar manner to isonarcotine, from hydrocotarnine and phthalaldehydic acid; it crystallises from alcohol, melts at 193°, gives a pale yellow coloration with concentrated sulphuric acid, and, in alcoholic solution, has an alkaline reaction. The *platinochloride* is pale yellow and flocculent. The *hydriodide*, $C_{20}H_{19}NO_5,HI$, crystallises in needles, and, like the *nitrate*, is sparingly soluble. J. B. T.

**Replacement of the Hydroxyl Group of the Cinchona Alkaloïds by Hydrogen.** By WILHELM KOENIGS (*Ber.*, 1895, **28**, 3143—3148).—When cinchonine chloride is dissolved in dilute sulphuric acid and treated with iron filings, a small amount of cinchene is formed along with *deoxycinchonine*, $C_{19}H_{22}N_2$, in which the chlorine atom of the cinchonine chloride is displaced by hydrogen. The base melts at 90—92°, and dissolves in alcohol, the solution being strongly dextrorotatory. It is not identical with dihydrocinchene. When heated with hydrobromic acid, additive products alone are formed, whilst with phosphoric acid, a little lepidine is produced. On oxidation with potassium permanganate in acid solution, it does not yield cinchoninic acid, but a product which appears to be derived from deoxycinchotenine, $C_{18}N_{20}N_2O_2$. *Deoxyconchinine*, $C_{20}H_{24}N_2O + 2H_2O$, prepared from conchinine chloride, crystallises in the asymmetric system, and melts at 80—82°. It is readily soluble in 10 per cent. aqueous tartaric acid, and does not yield apoquinine when heated with hydrobromic acid, an additive compound being the sole product. The base is thus sharply distinguished from conchinene, which melts at the same temperature. The alcoholic solution of the base is strongly dextrorotatory, and has a deep violet-blue fluorescence.

A. H.

**Resolution of Tropinic acid.** By RICHARD WILLSTÄTTER (*Ber.*, 1895, **28**, 3271—3292; compare this vol., i, 65).—*i*-Tropinic acid was prepared from tropine by Merling's method; the yield is 30—38 per cent., that of *d*-tropinic acid, from ecgonine, is 29 per cent. Both acids, when titrated, give values indicating their monobasicity; phenolphthaleïn was employed as indicator. *Methylic* i-*tropinate*, $C_8H_{11}NO_4Me_2$, is prepared by the action of hydrogen chloride on tropinic acid and methylic alcohol, and is a colourless, odourless, neutral oil; it boils at 268—272°, and is in part decomposed; potassium permanganate reacts slowly with it; when hydrolysed, tropinic acid is regenerated. The yield is 70—90 per cent. of the acid employed, but it is smaller if hydrogen bromide or sulphuric acid is used. The *aurochloride* is oily. The *picrate* crystallises in small, orange-yellow, quadratic prisms, melts at 121°, and is conveniently used for the purification of the methylic salt.

*Methylic* d-*tropinate* resembles the inactive compound; its *picrate* crystallises in long, thin needles melting at 120—121°.

*Methylic* i-*tropinate methiodide*, $C_8H_{11}NO_4Me_2,MeI$, is formed only slowly, and crystallises with $\frac{1}{2}H_2O$ from methylic alcohol in highly refractive, long prisms, from water in thin, prismatic aggregates, melting and decomposing at 172°, whilst, from ether, anhydrous, slender, nacreous plates are deposited. The *aurochloride* of the *methochloride* crystallises in thin, slender, golden, lustrous plates, and melts at 116—117°. When treated with silver oxide, the above methiodide yields a *betaïne* derivative,  $\begin{array}{l}\phantom{COOMe\cdot}CH_2\cdot CH_2\cdot CH—CO \\ \phantom{COOMe\cdot}| \qquad\qquad\ \ | \qquad\quad\ | \\ COOMe\cdot CH\cdot CH_2\cdot NMe_2\cdot O\end{array}$, the *aurochloride* of which crystallises in long, orange-yellow needles melting at about 182°. *Dimethylic* d-*tropinate methiodide* crystallises in colourless plates and needles, which melt and decompose at 177°. The *aurochloride* of the *methochloride* crystallises in microscopic, quadratic plates and needles melting at 114°; the corresponding derivative of the *betaïne*, is deposited in slender needles, which melt and decompose at 195°. Hofmann has shown that dimethylpiperylammonium iodide is decomposed by alkali into hydriodic acid and dimethylpiperidine; methylic *i*-tropinate methiodide behaves in a similar manner; when heated at 70—80° for two minutes with potassium carbonate, it yields *methylic* i-*methyltropinate*,

$$NMe_2{\cdot}CH{:}C(COOMe){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOMe,$$

which is a faintly coloured, oily liquid with an extremely feeble alkaline reaction; it boils at 280° (corr.), and decomposes in part under the ordinary pressure; potassium permanganate is instantaneously decolorised. The yield is about 90 per cent. of the theoretical. When fused with potash, first at 160°, and finally at 240—250°, it is converted into adipic acid, formic acid, dimethylamine, and, in small quantity, acetic acid. The yield of adipic acid is about 60 per cent. of the theoretical. Methylic *i*- and *d*-tropinate methiodide and methylic *d*-methyltropinate react in the same manner. *Methylic* i-*methyltropinate platinochloride*, $(C_{11}H_{10}NO_4)_2,H_2PtCl_6$, crystallises in orange-red, prismatic aggregates, and in well developed, highly refractive needles from water and hydrochloric acid respectively, and melts at 147—148°. The *aurochloride* is oily; the *picrate* is deposited in long, transparent, amber-coloured crystals melting at about 77—78°. *Methylic* i-*methyltropinate methiodide* crystallises in spherical, aggregated prisms melting at 131—132°; if deposited from alcohol, they contain $\frac{1}{2}H_2O$. The *aurochloride* of the *methochloride*,

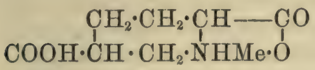
$$C_9H_{13}Me_2NO_4,MeAuCl_4,$$

forms well developed golden prisms melting at 118°, whilst the corresponding *monomethylic* derivative, $C_9H_{14}MeNO_4,MeAuCl_4$, crystallises in sulphur-yellow, prismatic aggregates, which soften at about 100°. *Methylic* d-*methyltropinate methiodide* resembles the inactive isomeride, and melts at 121—122°.

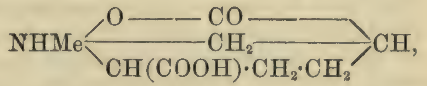
When methylic *i*- and *d*-methyltropinate methiodides are boiled with soda they yield trimethylamine, *piperylenedicarboxylic acid*, $CH_2{:}C(COOH){\cdot}CH_2{\cdot}CH_2{:}CH{\cdot}COOH$, and hydriodic acid, whilst a portion is resolved into its constituents; the reaction corresponds with that by which Hofmann prepared piperylene, $CH_2{:}CH{\cdot}CH_2{\cdot}CH{:}CH_2$, from the compound obtained by the complete methylation of piperidine. The acid crystallises from water in long, silky needles and prisms, melts at 169°, decomposes carbonates readily, rapidly decolorises potassium permanganate solution, and is dibasic; the electrolytic conductivity, $K = 0{\cdot}0116$, $\mu\infty = 354$. The yield is 75 per cent. of the theoretical. The *silver* salt, $C_7H_6O_4Ag_2$, is deposited in slender, microscopic prisms; under the same conditions, $\Delta'$ 1 . 2-pentenedicarboxylic acid yields a characteristic hydrogen silver salt. The *basic copper* salt is greenish-blue; the *lead* salt white and flocculent; the *zinc* salt is granular; the *cadmium* salt is crystalline. *Tetrabromopiperylenedicarboxylic acid*, $C_7H_8O_4Br_4$, crystallises from formic acid in colourless prisms, melts and decomposes at 218°, is stable towards potassium permanganate, and is rapidly decomposed by alkalis. The formation of this compound shows that piperylenedicarboxylic acid contains two double linkings, but their position remains undetermined.

*Propylic* i-*tropinate* is prepared in the same way as the methylic salt, which it resembles in general properties; the *methiodide* is oily;

the *aurochloride* of the *methochloride*, $C_8H_{11}Pr^{\alpha}_2NO_4,MeAuCl_4$, crystallises in slender, sulphur-coloured needles, and melts at 103°. When the above methiodide is treated with potassium carbonate, it yields *propylic* i-*methyltropinate*, the *methiodide* of which crystallises in lustrous, stellate needles and prisms melting at 116—117°; when it is heated with soda, piperylenedicarboxylic acid and trimethylamine are produced. The formation of the above methylic and propylic tropinate methiodides shows that tropinic acid contains a tertiary nitrogen atom, as indicated by Merling's formula; Ladenburg's formula indicates the presence of a secondary nitrogen atom. The production of adipic acid from methyltropinic acid, described above, is probably preceded by that of formyladipic acid, $OH\cdot CH\dot{:}C(COOH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$, which is then further hydrolysed to adipic and formic acids. The monobasicity of tropinic acid suggests that it may be a betaïne derivative,



or



but the methylic and propylic salts have not this constitution, since the latter, after complete methylation, yields trimethylamine, and not dimethylpropylamine. J. B. T.

**Cactus Alkaloïds. II.** By ARTHUR HEFFTER (*Ber.*, 1896, **29**, 216—229; compare Abstr., 1895, i, 120).—The formula, $C_{13}H_{19}NO_3$, is now assigned to pellotine, and its *mercurochloride* has been prepared. Its third oxygen atom must exist in the form of hydroxyl, for it yields an oily *monobenzoyl* derivative, the *platinochloride* and *aurochloride* of which were prepared. When boiled with methylic iodide and methyl-alcoholic potash, the alkaloïd yields *methylpellotine methiodide*, $C_{14}H_{21}NO_3,MeI$, melting at 225°; from this, the *chloride* and *platinochloride* were prepared; the quaternary *ammonium base* itself forms hygroscopic crystals which melt at 185°. No well defined products were obtained by heating the alkaloïd with hydrochloric acid; in one experiment, the compound $C_{11}H_{12}N(OH)_2\cdot OMe$—pellotine with one of its two methoxyl groups replaced by hydroxyl—was obtained, and characterised by means of its yellow *picrate*, which melts at 93°. Of the products obtained by distilling the alkaloïd with soda lime or zinc dust, only trimethylamine could be identified; of the products of its oxidation, only oxalic acid.

Alkaloïds of *Anhalonium Lewinii*, Hennings (*Lophophora Lewinii*, Rusby).—The dried "discs" (*Scheiben*) of this cactus are used by the Indians of N. Mexico for the preparation of an intoxicant, and are brought into commerce under the name of "Muscale buttons" (from Spanish *Mezcàl*, a kind of brandy made from various species of *Agave*). They were extracted with 70 per cent. alcohol, and the residue obtained by evaporating this extract was extracted with ether and then with chloroform. The chloroform dissolved an alkaloïd which was named *mezcaline*, whilst the ether dissolved several alkaloïds, and by crystallising their sulphates, the sulphate of one, *anhalonidine*, was obtained mixed with some mezcaline sulphate. The mother liquor was treated with barium chloride, and the hydrochloride of *anhalonine* (Lewin, this vol., i, 194) then obtained from it. From the final mother liquor, the mercurochloride of another alkaloïd, *lophophorine*, was obtained and eventually converted into the crystallised *hydrochloride*.

*Mezcaline*, $C_{11}H_{17}NO_3$, melts at 151°; it contains three methoxyl groups. The *sulphate* has the composition $(C_{11}H_{17}NO_3)_2,H_2SO_4 + 2H_2O$; the yellow *platinochloride* is anhydrous.

*Anhalonidine*, $C_{12}H_{15}NO_3$, melts at 160°, and contains two methoxyl groups; the *hydrochloride* is lævorotatory in solution; the yellowish-red *platinochloride* is anhydrous.

Anhalonine, $C_{12}H_{15}NO_3$, melts at 85·5° (Lewin, 77·5°); it contains one methoxyl group.

*Lophophorine*, $C_{13}H_{17}NO_3$, was not obtained crystallised; the yellow *platinochloride* is anhydrous.

All give the same colour reactions, identical with those of pellotine. The following percentages of the pure alkaloïds were obtained from the drug: mezcaline, 6·3; anhalonidine (with a little mezcaline), 5·3; anhalonine, 3·0; lophophorine, 0·5. C. F. B.

**Pectase.** By GABRIEL BERTRAND and ALFRED MALLEVRE (*Compt. rend.*, **121**, 726—728).—See this vol., ii, 267.

**The Separation of Lysine.** By EDMUND DRECHSEL (*Ber.*, 1895, **28**, 3189—3190).—Lysine may be isolated from the products of the decomposition of caseïn by hydrochloric acid, by converting it first into the dibenzoyl compound, lysuric acid. This is then purified by the recrystallisation of its *acid barium salt*,

$$2C_6H_{12}Bz_2N_2O_2 + (C_6H_{11}Bz_2N_2O_2)_2Ba,$$

from which the pure lysine can readily be liberated. A. H.

# Organic Chemistry.

**Sodium Nitrosoferrocyanide.** By Karl A. Hofmann (*Zeit. anorg. Chem.*, 1896, **11**, 278—287).—The *salt*, $FeC_5N_6O_2Na_4H,10H_2O$, is obtained by treating an aqueous solution of sodium nitrosoferrocyanide with sodium hydroxide. On adding alcohol to the reddish-yellow solution thus obtained, a yellow syrup is precipitated; it is dissolved in water and again precipitated with alcohol, and then allowed to crystallise in a vacuum over sulphuric acid. Care must be taken to exclude carbonic anhydride, and to maintain the temperature below 15°, for in the presence of carbonic anhydride, sodium nitrosoferrocyanide is re-formed, and at temperatures above 15° decomposition takes place with formation of sodium ferrocyanide, ferric hydroxide, and sodium nitrite. It crystallises in beautiful, yellowish-red, monosymmetric tablets very similar to those of potassium ferricyanide; $\beta = 98—100°$. It is very easily soluble in water, gives a dark red coloration with ammonium sulphide, and when dried at 110°, yields a yellow powder which is completely soluble in water. The *silver salt*, $FeC_5N_6O_2Ag_4H,2H_2O$, is obtained by adding a solution of the sodium salt to a solution of silver nitrate containing ammonium nitrate. It loses its water of crystallisation at 90°.

*Methylic nitrosoferrocyanide*, $Fe(CN)_5NOMeH_2,2H_2O$, is obtained by treating an ice-cold mixture of sodium nitrosoferrocyanide and methylic alcohol with hydrogen chloride, and concentrating the solution in a vacuum over potassium hydroxide and sulphuric acid. It crystallises in red nodules, is easily soluble in water and dilute sodium hydroxide with a reddish-yellow coloration, and gives a characteristic bluish-violet coloration with ammonium sulphide. The *ethylic compound*, obtained in a similar way, crystallises in small, lustrous, bright red plates with $3H_2O$, and gives the nitrosoferrocyanide reactions with alkali carbonates and ammonium sulphide. The *propylic compound*, with $3H_2O$, crystallises in bright red aggregates, which quickly turn green on exposure to air. From the formation of the above compounds, the author concludes that the nitrosoferrocyanide contains an oximido-group as expressed in the formula

$$Fe(CN)_5H_2\!:\!NOH.$$

E. C. R.

**Composition of the Ohio and Canadian Sulphur Petroleums.** By Charles F. Mabery (*Amer. Chem. J.*, 1895, **17**, 713—748).—The constituents were separated by distillation in an apparatus somewhat resembling that used in Warren's classical research, but the fractionation was effected under reduced pressure, the latter being regulated by means of an adjustable artificial leak. Ohio petroleum is intermediate in properties between Caucasian and Pennsylvanian oils, and contains the following paraffinoïd hydrocarbons: Two butanes (b. p. = 0° and 7—9°), pentane and isopentane, hexanes, and heptanes, together with octane and nonane. These form less than one-tenth of the oil, and correspond with those present in Pennsylvanian oils, of which they form about one-fifth (see next abstract). A. L.

## Composition of the Ohio and Canadian Sulphur Petroleums.

By Charles F. Mabery (*Amer. Chem. J.*, 1896, **18**, 43—79; compare Abstr., 1894, i, 266, and preceding abstract).—The principal features of the Ohio sulphur petroleum are: (1) The crude oil is heavier than the Pennsylvanian, and lighter than the Russian oil. In the quantities of the higher distillates, and in its general properties it more nearly resembles the latter than the former. (2) It differs from other petroleums in the large amounts of sulphur compounds, which affect its general properties. (3) It resembles the Pennsylvania oil in containing, below 150°, members of the series $C_nH_{2n+2}$, although in much smaller quantities. The presence of the two isomeric series, $C_nH_{2n+2}$, in the Ohio oil confirm the observations of Warren on the Pennsylvania petroleum. (4) The aromatic hydrocarbons are present in minute quantities, apparently much smaller than in other petroleums. Benzene, toluene, and meta- and para-xylene have been identified. The hexahydro-series, $C_nH_{2n}$, is represented by hexahydroisoxylene, and very probably by higher members. Hexahydrobenzene and hexahydrotoluene are not present. (5) By the formation of characteristic nitro-products, and from the results of bromine absorption, the presence in the crude oil of unsaturated hydrocarbons, $C_nH_{2n}$, seems to be indicated.

The characteristic qualities of the Canadian petroleums are summarised as follows: (1) In its high specific gravity and in the proportions which distil at different temperatures, Canadian petroleum approaches the Russian oil more nearly than it approaches the Ohio petroleum, but the specific gravity of the distillates is lower than that of the Russian distillates. As indicated by its lower specific gravity, Oil Springs oil is essentially different from the Petrolia oil. This is especially evident in the lower percentage of sulphur, the larger quantities of the distillates, the higher specific gravity of these distillates, and the higher bromine absorption. (2) Petrolia oil is composed principally, below 150°, of members of the series $C_nH_{2n+2}$, although in much smaller quantities even than in Ohio oil (*sic*). Another series is present capable of forming nitro-products resembling the nitro-compounds of the series $C_nH_{2n+2}$, or the unsaturated hydrocarbons $C_{2n}H_n$ (*sic*). (3) Benzene, toluene, and para- and meta-xylene are present in minute proportions. The hexahydro-series is represented by hexahydroisoxylene, and probably by higher members. (4) The presence of hydrocarbons capable of forming additive products is indicated by the behaviour of the distillates towards bromine, as well as the formation of unsaturated hydrocarbons in the distillates above 200° or 250°, due to cracking. (5) As in Ohio oil, the sulphur compounds have a tendency to collect in the higher fractions.

The paper concludes with some remarks on the origin of petroleum, and it is shown that the limestone petroleums in general contain a higher percentage (up to 0·35 per cent.) of nitrogen than other petroleums do. A. G. B.

**Combustion of Acetylene.** By HENRI L. LE CHATELIER (*Compt. rend.*, 1895, **121**, 1144—1147).—The combustion of acetylene was investigated by the methods previously employed by the author and Mallard with other gases. Mixtures of acetylene and air containing less than 7·74 per cent. of the former burn completely to carbonic anhydride and water, with a yellowish flame of low illuminating power. With proportions of acetylene between 7·74 and 17·37 per cent., the flame is pale blue with a feeble yellowish aureole, and hydrogen and carbonic oxide are amongst the products of combustion, the relative proportions of these gases being represented by the same formula of equilibrium as in the case of other combustible gases. With more than 17·37 per cent. of acetylene, the reactions are incomplete, and free carbon and unburnt acetylene are present in the gases from the flame as well as hydrogen and carbonic oxide, the flame being red and smoky. The lower and upper limits of combustibility are, with oxygen, 2·8 and 93 per cent. of acetylene respectively, and with air 2·8 and 65 per cent. In a tube 40 mm. in diameter, the velocity of propagation of the flame is 0·1 metre per second with 2·9 per cent. of acetylene, but increases rapidly with the proportion of acetylene until the latter is 8 per cent., when the velocity is 5 metres per second, and afterwards it increases slowly to a maximum of 6 metres per second with 9 to 10 per cent. of acetylene, and beyond this limit it decreases rapidly. The temperature of ignition is only 480°, and hence explosive mixtures of acetylene can be ignited in glass tubes heated with a spirit lamp. The calculated temperature of combustion with 7·74 per cent. of acetylene is 2420°, with 12·2 per cent. 2260°, and with 17·37 per cent. 2100°. When burnt with its own volume of oxygen, the temperature of the flame should be 4000°.

C. H. B.

**Homolinalol.** By FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1896, **29**, 691—695; compare Abstr., 1895, i, 646).—*Homolinalol*,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(OH){\cdot}CH_2{\cdot}CH{:}CH_2,$$

is obtained by slowly adding a mixture of allylic iodide and methylheptenone to granulated zinc in a flask surrounded by a freezing mixture; after remaining at low temperatures during three days, the product is distilled in an atmosphere of steam, homolinalol being separated from the distillate by converting it into the *acetate*, a liquid which boils at 111—117° under a pressure of 15 mm. Homolinalol boils at 102—104° under a pressure of 14 mm., and has an odour which suggests linalol; the sp. gr. = 0·8618 at 20°, and the refractive index $n_D$ = 1·46534 at the same temperature, whence the molecular refraction M = 53·92. When homolinalol is rapidly heated with camphoric or succinic anhydride, it yields the *hydrocarbon* $C_{11}H_{18}$, which boils at 182—185°, has the sp. gr. 0·8415 at 16°, and the refractive index $n_D$ = 1·47292, whence the molecular refraction M = 50·00. Agitation with 10 per cent. sulphuric acid converts homolinalol into a *compound* which boils at 135—136° under a pressure of 11 mm. Oxidation with potassium permanganate followed by chromic anhydride and sulphuric acid gives rise to acetone and a small quantity of levulinic acid, along with an acid which is probably methylhydroxyadipic acid,

$$COOH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot COOH.$$

M. O. F.

**Compounds of Sugars with Ethylene Mercaptan, Trimethylene Mercaptan, and Benzyl Mercaptan.** By WILLIAM T. LAWRENCE (*Ber.*, 1896, **29**, 547—552; compare Abstr., 1894, i, 269).—*Glucose-ethylenemercaptal*, $C_6H_{12}O_5\colon S_2C_2H_4$, is obtained by agitating ethylene mercaptan with a solution of glucose in hydrochloric acid (sp. gr. 1·19); it has a bitter taste, and crystallises from alcohol in colourless, slender needles melting at 143° (uncorr.). Three parts of boiling water dissolve the mercaptal, which is soluble in 12 parts of water at common temperatures, separating from a 10 per cent. solution in pyramids; the specific rotatory power $[\alpha]_D = -10·81°$ in aqueous solution at 20°. The mercaptal is indifferent towards dilute acids, but is readily decomposed by bromine, which gives rise to diethylenic tetrasulphide and glucose.

*Mannose-ethylenemercaptal* melts at 153—154° (uncorr.), and has the specific rotatory power $[\alpha]_D = +12·88°$ at 20°. *Galactose-ethylenemercaptal* melts at 149° (uncorr.), and does not crystallise readily; *arabinoseethylenemercaptal* melts at 154° (uncorr.), and dissolves in 8 parts of water. *Rhamnose-ethylenemercaptal* crystallises from alcohol in slender, colourless needles, and melts at 169° (uncorr.); *xylose-ethylenemercaptal* resembles the derivatives of glucose and rhamnose.

*Glucose-trimethylenemercaptal*, $C_6H_{12}O_5\colon S_2C_3H_6$, crystallises from alcohol in slender needles, which taste bitter and melt at 130°; it dissolves in 1½ parts of boiling water and 15 parts of boiling alcohol, being soluble in 9 parts of water at the ordinary temperature. *Arabinosetrimethylenemercaptal* crystallises in long needles, has a bitter taste, and melts at 150° (uncorr.); *galactose-trimethylenemercaptal* and *xylose-trimethylenemercaptal* are colourless syrups.

*Glucose-benzylmercaptal*, $C_6H_{12}O_5(SCH_2Ph)_2$, crystallises from 50 per cent. alcohol in slender, white needles, and melts at 133° (uncorr.); it has a bitter taste, and dissolves in 8 parts of boiling alcohol, but requires 50 parts of boiling water. *Galactose-benzylmercaptal* melts at 130° (uncorr.), and dissolves in 6 parts of hot alcohol; *rhamnose-benzylmercaptal* crystallises in plates, and melts at 125°. *Arabinose-benzylmercaptal* crystallises from 50 per cent. alcohol in very long needles, and melts at 144°; *xylose-benzylmercaptal* is a syrup.

M. O. F.

**Crystallised *d*-Mannose.** By W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1895, **14**, 329).—The author has obtained *d*-mannose crystallised in the form of prisms, which are only slightly hygroscopic; its aqueous solution shows multirotation, at first being lævogyrate, but afterwards dextrogyrate.

J. J. S.

**Crystallised Anhydrous Rhamnose.** By EMIL FISCHER (*Ber.*, 1896, **29**, 324—325).—Tanret (*Compt. rend.*, 1896, **122**, 86) has overlooked the fact that the author has already prepared this substance by heating ordinary rhamnose on the water bath and crystallising the product from acetone (Abstr., 1895, i, 440). In 10 per cent. aqueous solution at 20°, the specific rotation is $[\alpha]_D = +31{\cdot}5$ one minute after the substance has been dissolved; after half an hour, it is only + 18°, and it sinks eventually to the value generally ascribed to rhamnose. C. F. B.

**Volemitol, a new Saccharine Matter.** By EMILE E. BOURQUELOT (*J. Pharm.*, 1895, [6], **2**, 385—390).—To prepare volemitol (Abstr., 1895, i, 639), 500 grams of the dried fungus *Lacterius volemus* is digested for 20 minutes, on a water bath, with two litres of 85° alcohol, or, if the fresh fungus is used, 95° alcohol is employed; the hot alcohol is decanted, the digestion repeated with 1·5 litre of fresh alcohol and the residue pressed. The combined liquors are filtered when cold, the alcohol distilled off, and the residue concentrated to a syrup which is extracted with 95° alcohol; from this solution, volemitol is very slowly deposited. It is purified by dissolving it in boiling 80° alcohol, using 8 parts of solvent to 1 of volemitol, filtering, warming, allowing to crystallise, drying with the air pump, and washing first with 95° alcohol, then with ether, and finally drying at 60°. Volemitol forms little spherical accumulations of minute, fine, white, soluble needles, the melting point, specific rotation, &c., for a pure sample are given in the abstract referred to. It contains no water of crystallisation, and decomposes when heated above 200°, evolving water and an odour of caramel. It is faintly sweet, is very soluble in water, but only slightly so in alcohol; the solubility, in the latter case, however, being increased by the presence of certain organic compounds. It does not reduce Fehling's solution even after treatment with boiling dilute sulphuric acid, nor is it fermented by yeast. It prevents the precipitation of copper oxide by alcohol, but produces a blue precipitate in ammoniacal copper sulphate. The author has not obtained any nitro-derivative, and when digested at the boiling point for 1¼ hour with anhydrous sodium acetate, and acetic anhydride, it yields a crystalline compound having the properties of mannitol hexacetate, but, unlike mannitol, when digested only 20 minutes, no crystalline product is obtained. With acetaldehyde and benzaldehyde, it forms acetals, which crystallise in silky needles. The ethylic acetal is very soluble in boiling 75° alcohol; it melts at 190° and is lævorotatory. D. A. L.

**Dextrins obtained by the Hydrolysis of Starch.** By K. BÜLOW (*Pflüger's Archiv*, 1895, **62**, 131—155).—The author has obtained amylodextrin by adding pure potato starch in small quantities to an equal weight of potash dissolved in water. The mixture is warmed on the water bath, and finally, for about 10 minutes, over a free flame; the amylodextrin may then be precipitated by alcohol, and if the directions are carefully followed, it is obtained in the form of a colourless powder which can easily be filtered off. It is best purified by repeated solution in hot water and precipitation by absolute alcohol, when it is obtained in the form of a white solid which, when quite free from alcohol, is not affected by exposure to air. It is only sparingly soluble in water, even when hot, and yields an opalescent solution, from which after a time, a portion of the dextrin separates. With iodine solution, it gives a blue coloration, and does not reduce Fehling's solution, even on boiling with it for some time.

The author has also obtained amylodextrin from starch by digesting it at 60° for 10—15 minutes with a chloroform solution of diastase. If the digestion is continued for too long a time, erythrodextrin is obtained together with amylodextrin. Attempts to separate the two dextrins by means of fractional precipitation with baryta solution proved useless, the method of dialysis is also too slow for the separation of the two, but may be used for the detection of erythrodextrin in a sample of amylodextrin. Both amylodextrins were partially precipitated by barium hydroxide solution and the precipitate analysed. The precipitate obtained from the amylodextrin from potato starch had the composition: Dextrin : $Ba(OH)_2$ = 100 : 13·25, which agrees well with the formula $(C_6H_{10}O_5)_8,Ba(OH)_2$.

Amylodextrin obtained from starch by means of dilute sulphuric acid has the same properties as that obtained by means of potash or diastase; but all three differ materially from the amylodextrin described by Lintner and Düll (Abstr., 1894, i, 5), especially as regards their solubility in hot water. The author considers his compound to be pure amylodextrin, and thinks that the substance described by Lintner and Düll is merely a mixture of his amylodextrin with erythrodextrin. A half per cent. solution of amylodextrin in water is immediately gelatinised when treated with a 20 per cent. sodium hydroxide solution. The gelatinised mass becomes liquid on warming, but again solidifies on cooling, and is readily soluble in cold water. Potassium hydroxide does not act in the same way.

*Erythrodextrin* was prepared by treating starch paste with diastase at 60—70° until it gave a clear red coloration with iodine. After destroying the diastase by boiling and evaporating, the erythrodextrin was precipitated by means of alcohol, and freed from achroodextrin by treatment with excess of barium hydroxide, whereby the barium compound of erythrodextrin was thrown down while the achroodextrin remained in solution. The erythrodextrin was also prepared by slightly modified methods, but in all cases it forms a snow-white powder, which is not altered when exposed to air. It is readily soluble in water, yields a brownish-red coloration with iodine solution, and does not reduce alkaline copper sulphate solution at the ordinary temperature. The solution was precipitated with an insufficient quantity of barium hydroxide, when a compound was obtained, probably having the formula $(C_6H_{10}O_5)_5,Ba(OH)_2$, or $(C_6H_{10}O_5)_6,Ba(OH)_2$. The rotatory power in all cases is about $[\alpha]_D = 190$, even when the erythrodextrin is mixed with achroodextrin.

Achroodextrin was obtained by treating starch paste with diastase at 60—70° until it remained colourless when treated with iodine: After boiling to destroy the diastase, it was precipitated by 96 per cent. alcohol. It forms a snow-white powder readily soluble in water and is not precipitated from its aqueous solution by barium hydroxide, but can be precipitated in this way from an alcoholic solution, yielding a compound $(C_6H_{10}O_5)_4,Ba(OH)_2$. Its specific rotatory power is $[\alpha]_D = + 179—184°$, and it readily reduces Fehling's solution.

Attempts to further purify the achroodextrin (1) by treatment with phenylhydrazine, (2) by partial oxidation with alkaline copper sulphate solution, (3) by Landwehr's iron precipitation method proved fruitless, but the author thinks that it is quite possible either by fractional precipitation with barium hydroxide in a 10 per cent. alcoholic solution, or by dialysis, or by a combination of both methods, to prepare an achroodextrin with constant properties and finally to make a molecular weight determination. J. J. S.

**Reduction Products of Methylbutylnitramine.** By Antoine P. N. Franchimont and H. van Erp (*Rec. Trav. Chim.*, 1895, **14**, 317—326; compare Abstr., 1885, 963).—A mixture of methylbutylamine and methylbutylhydrazine was obtained by reducing methylbutylnitramine with zinc dust and acetic acid. The two are best separated by treatment with ethylic oxalate, since the hydrazine yields oxalmethylbutylhydrazide and the amine methylbutyloxamic acid.

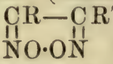
*Oxalmethylbutylhydrazide*, $C_2O_2(NH{\cdot}NMe{\cdot}C_4H_9)_2$, is a colourless, crystalline substance; it melts at 156°, and is moderately soluble in boiling alcohol. When boiled with aqueous potash and then distilled, it yields *methylbutylhydrazine*, which boils at 50·5—51° under 38 mm. pressure; it is a colourless liquid, of sp. gr. = 0·8092 at 15°, and is miscible in all proportions with water, alcohol, and ether. Its *hydrochloride* is extremely hygroscopic, and therefore difficult to prepare, and its *platinochloride* does not crystallise readily. When an ethereal solution of the hydrazine is treated with yellow mercuric oxide, it yields *methylbutyltetrazone;* this distils at 119—120° under 18 mm. pressure, and is a colourless liquid of sp. gr. = 0·8798 at 15°. It is only sparingly soluble in water, has an alkaline reaction, and does not reduce Fehling's solution. The mother liquors from the oxalmethylbutylhydrazide were treated with nitrous acid, in order to convert any of the hydrazine into methylbutylamine, and, after dilution with water, were distilled.

*Methylbutylamine* is a colourless liquid with a slight ammoniacal odour, and is readily soluble in water, alcohol, and ether. It has a sp. gr. = 0·7375 at 15°, boils at 90·5—91·5° under 764 mm. pressure, and does not reduce Fehling's solution. The authors contradict Zublin's statement (Abstr., 1878, 284) that normal butylamine reduces Fehling's solution. The *hydrochloride*, $NHMe{\cdot}C_4H_9,HCl$, crystallises in small plates, melts at 170—171°, is extremely hygroscopic, and is soluble in water, alcohol, and chloroform. The *platinochloride* is readily soluble in water, sparingly in alcohol, and melts at 203°, at the same time undergoing decomposition.

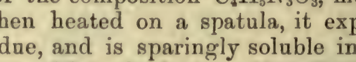
*Methylbutylnitrosamine* is a yellow liquid, only slightly soluble in water, but miscible with alcohol and ether; its sp. gr. = 0·936 at 15°, and it boils at 84—85° under 15 mm. pressure, and at 199—201° under 767 mm. pressure. J. J. S.

**Action of Fused Potash on Methylnitramine and Dimethylnitramine.** By H. van Erp (*Rec. Trav. Chim.*, 1894, **14**, 327—328, and *Ber.*, 1896, **29**, 474—476).—When dimethylnitramine is fused with potash, it yields potassium nitrite and ethylamine, which was recognised by conversion into dinitromonomethylaniline. Methylnitramine, when treated in a similar manner, yields a mixture of hydrogen and ammonia, together with formic and nitrous acids. These results are at variance with the statements of Thiele and Lachmann (Abstr., 1895, i, 587), according to whom the nitramines yield nitric acid and methylamine and dimethylamine respectively.

A. H.

**Dimethylglyoxime.** By ENRICO RIMINI (*Gazzetta*, 1895, **25**, ii, 266—268).—The glyoxime peroxides,  $\begin{array}{c}CR—CR'\\ \| \qquad \| \\ NO\cdot ON\end{array}$, on reduction with tin and hydrochloric acid, yield furfurazinic derivatives, whilst, on reduction with zinc dust and acetic acid, they give syn-dioximes. Dimethylglyoxime peroxide, when treated with zinc dust and acetic acid, yields the dimethylglyoxime obtained by Fittig (Abstr., 1889, 490) by the action of hydroxylamine on diacetyl. This glyoxime is therefore a syn-glyoxime, as is also indicated by the readiness with which it yields dimethylazoxazole (Wolff, Abstr., 1895, i, 182).

W. J. P.

**Action of Hydroxylamine Hydrochloride on Glyoxal.** By ARTURO MIOLATI (*Gazzetta*, 1895, **25**, ii, 213—217).—On preparing glyoxime by the action of hydroxylamine on glyoxal in acid solution, the crude product contains a certain proportion of an explosive *substance*, which is obtained pure by evaporating a concentrated solution of hydroxylamine hydrochloride and glyoxal until crystallisation begins, and then neutralising exactly with sodium carbonate; the crystalline precipitate is extracted with ether to remove glyoxime, and crystallised from boiling water, when colourless needles are obtained of the composition $C_4H_5N_3O_3$, melting and decomposing at 176°. When heated on a spatula, it explodes like guncotton, leaving no residue, and is sparingly soluble in cold water, alcohol, or ether; it is readily soluble in acids, alkalis, or alkali carbonates, but is precipitated unaltered on carefully neutralising the solution. It is slowly decomposed when boiled with acetic anhydride or chloride. It yields a *benzoyl* derivative, which was not analysed; its *hydrochloride*, $C_4H_5N_3O_3,HCl$, crystallises in needles melting at the same temperature as the base, and the *platinochloride* is very soluble in water and explodes on heating. The base probably has the constitution  $CH<\begin{array}{c}C(NOH)\\ N\text{———}O\end{array}>CH\cdot CH:NOH$, and is not formed by the action of hydroxylamine on glyoxal in neutral or alkaline solutions, therefore glyoxime should be capable of being prepared under such conditions.

W. J. P.

**Action of Halogens on Formaldehyde.** By ANDRÉ BROCHET (*Compt. rend.*, 1895, **121**, 1156—1159),—Dry chlorine has no action on trioxymethylene in diffused daylight at the ordinary temperature, but, on gently heating, hydrogen chloride and carbonic oxide are given off. In direct sunlight, carbonic chloride is also formed, but it is a secondary product, resulting from the action of excess of chlorine on carbonic oxide, and the quantity produced is greater the more rapid the current of chlorine.

A mixture of 1 gram of trioxymethylene and 1 c.c. of bromine at the ordinary temperature forms a dry powder, which, when allowed to remain at the ordinary temperature in the dark or in diffused daylight, gradually liquefies and acquires a blood-red colour. In sunlight, these changes are much more rapid, but in both cases a gas is liberated which contains a high proportion of carbonic oxide. At 100°, the solid mixture liquefies at once, but gas is only very slowly liberated, and it contains a lower proportion of carbonic oxide with some carbonic anhydride. In all these cases, some carbonic bromide is formed, probably as a result of the action of bromine on the carbonic oxide.

In all cases, the action of chlorine or bromine on formaldehyde produces carbonic oxide, and this result explains the occurrence of carbonic oxide in the products of the action of halogens on methylic alcohol (Abstr., 1895, i, 637).

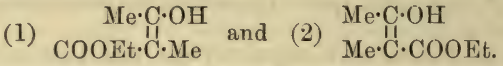
When methylic alcohol is burnt with a limited quantity of oxygen, from 5 to 10 per cent. is converted into formaldehyde, and from 3 to 5 per cent. into carbonic oxide, whilst the rest is completely burnt to carbonic anhydride and water. C. H. B.

**Tetrinic [Tetric] acid.** By Paul C. Freer [and, in part, E. R. Miller] (*Amer. Chem. J.*, 1895, **17**, 779—726).—The author's results are not in accordance with those of Nef (see Abstr., 1892, 140). The product of bromination of ethylic methylacetoacetate or its sodium derivative is not a single substance, and contains unaltered ethylic methylacetoacetate, and ethylic α- and γ-monobromo- and dibromomethylacetoacetates. It may be partially resolved by distillation, the different fractions yielding, under the same conditions, different proportions of tetric acid. On oxidising the mixture by cold alkaline permanganate, a small quantity of oxalic acid is obtained, together with chloracetic acid and much acetic acid, the first two obviously being produced by the oxidation of the γ-bromo-derivative, and the latter from the β-derivative. The total amount of γ-derivative present in a specimen prepared by the author is estimated at 6 per cent., a specimen prepared from Kahlbaum's ethylic methylacetoacetate containing much less.

The isomeric ethylic bromomethylacetoacetates may be partially separated by means of alkalis, in which the α-derivative is insoluble; after treatment in this mannor, the α-derivative yielded no tetric acid, the presence of hydrobromic acid being necessary to effect an initial change to the γ-derivative, which alone affords tetric acid when distilled or heated.

Ethylic bromomethylacetoacetate, on being heated at 100° for some time, yields 87·4 per cent. of the theoretical quantity of tetric acid, and a small quantity of hydrogen bromide may be detected in the liberated gases.

As different samples of apparently pure ethylic methylacetoacetate differ in behaviour when brominated, it is possible that there exist together the geometric isomerides



$$(1)\ \begin{matrix}\mathrm{Me{\cdot}C{\cdot}OH}\\ \|\\ \mathrm{COOEt{\cdot}C{\cdot}Me}\end{matrix}\quad \text{and}\quad (2)\ \begin{matrix}\mathrm{Me{\cdot}C{\cdot}OH}\\ \|\\ \mathrm{Me{\cdot}C{\cdot}COOEt.}\end{matrix}$$

(1) would give a γ-derivative which would readily evolve ethylic bromide and yield tetric acid; (2) would merely change gradually by molecular re-arrangement.

With E. R. Miller.—Contrary to Demarçay's account, silver tetrate is fairly soluble in water, and is used for the preparation of ethylic tetrate, the vapour density of which, at 174°, agrees with the formula $C_5H_5O_3Et$. The *benzoyl* derivative of tetric acid, obtained by the action of benzoic chloride on sodium tetrate, separates from acetone in long, lustrous needles, melting at 128°, and is partially decomposed by boiling alcohol, ethylic benzoate being formed. Its molecular weight in boiling benzene is normal. *Tetric chloride*, contrary to the statements of Wolff (this vol., i, 887), is capable of existence, and has a normal vapour density; it dissolves slowly in alkalis, thus evincing its lactonic character. As in the case of ethylic tetrate, a liquid and a solid modification have been obtained. A. L.

**Action of Inorganic acidic Metallic Oxides on Organic acids.** By Arthur Rosenheim [and, in part, Ludwig Cohn] (*Zeit. anorg. Chem.*, 1896, **11**, 175—222; see also Abstr., 1893, i, 626).—I. *Aluminium Oxalates* [with Ludwig Cohn].—When a solution of oxalic acid is saturated with an excess of alumina and the filtrate evaporated on the water bath, a clear, pale yellow syrup is obtained, which contains the compound $Al_2O_3,3C_2O_3$. It cannot be obtained in crystals, gives no precipitate when treated with alcohol or ether, solidifies to a homogeneous, white mass when cooled to $-15°$, and melts again at $-5°$. It gives no reaction with vanadic acid, showing that it contains no free oxalic acid, gives an acid reaction towards indicators, and when boiled with ammonia is decomposed, with formation of a complex ammonium salt and precipitation of about half the aluminium as hydroxide. With chlorides of the metals, it forms well-characterised compounds containing alumina. The *barium salt*, $Al_2Ba_3(C_2O_4)_6 + 6H_2O$, crystallises in silky, lustrous needles, and is partially decomposed on recrystallisation.

A *double salt*, of the composition $Al_2K_6(C_2O_4)_6 + 5H_2O$, is obtained by treating a boiling solution of acid potassium oxalate with excess of alumina; it crystallises in large, colourless, prismatic needles, gives most of the reactions for aluminium, except that only part of the aluminium is precipitated by boiling with ammonia. With calcium chloride, it yields a compound containing aluminium, and calcium oxalate is not precipitated. The corresponding sodium and ammonium salts, with $9\frac{1}{2}$ and $5\frac{1}{2}$ $H_2O$ respectively, are obtained in a similar manner. The salts are likewise obtained by treating the above aluminium oxalate with the corresponding chlorides. They give up their water of crystallisation when heated at 80—90°, and do not reduce vanadic acid.

A *salt*, of the composition $2\frac{1}{2}K_2O,Al_2O_3,5C_2O_3,5H_2O$, is obtained by saturating a boiling solution of acid potassium oxalate with excess of alumina, concentrating the solution in presence of excess of alumina over a bare flame, and, after rapid filtration, evaporating it to crystallisation; it forms rhombic scales, and decomposes on recrystallisation. The *sodium salt* with $8H_2O$ separates in nodules or rhombic crystals, and effloresces rapidly on exposure to air. The *ammonium salt* was not obtained, as the solution on concentration gives off ammonia and the salt $3(NH_4)_2O,Al_2O_3,6C_2O_3,5\frac{1}{2}H_2O$, then separates. These salts contain one-OH group, as shown by the fact that the last $\frac{1}{2}$ mol. of water is only given off at 130°. They dissolve vanadic acid with a yellow coloration, have a neutral reaction, and give crystalline precipitates of double aluminium oxalates when treated with chlorides of the alkaline earths. When dissolved in water, they decompose according to the equation $3OH{\cdot}Al_2(OOC{\cdot}COOR)_5 = 5Al(OOC{\cdot}COOR)_3 + Al(OH)_3$, and can therefore only be obtained in the presence of an excess of alumina.

The *salt* $2K_2O,Al_2O_3,4C_2O_3,3H_2O$ is obtained by slowly adding potassium hydroxide (1 mol.) to a solution of acid potassium oxalate (5 mols.) saturated with alumina. It crystallises in rhombic scales, and is easily soluble in cold and warm water, but these solutions at once decompose with separation of alumina. The *sodium* salt with 6 and $7H_2O$ crystallises in small plates. The *ammonium* salt crystallises with $2H_2O$. These salts give similar reactions to the preceding, and contain $1H_2O$ more intimately combined. Salts more basic than the above cannot be obtained. When a solution containing the constituents in the proportion $2\frac{1}{2}R_2O,Al_2O_3,5C_2O_3$ is treated with 2 or 3 mols. of potassium hydroxide, alumina is precipitated, and the preceding salts, together with normal oxalates, are obtained.

The *salt* $K_2O,Al_2O_3,4C_2O_3,7\frac{1}{2}H_2O$ is obtained by adding to a filtered solution of oxalic acid (3 mols.), saturated with alumina, a concentrated solution of normal potassium oxalate (1 mol.) evaporating to a syrup, and then stirring well with a glass rod. The salt crystallises in microscopic tablets, and can be recrystallised without decomposition. The *sodium* and *ammonium* salts are similar, and crystallise with $10\frac{1}{2}$ and 5 $H_2O$ respectively. These salts give a faintly acid reaction, do not react with vanadic acid, and give crystalline double aluminium oxalates when treated with chlorides of the alkaline earths. Only part of the aluminium is precipitated by boiling with ammonia.

II. *Alkali Chromium Oxalate.*—When a boiling solution of oxalic acid is saturated with an excess of freshly precipitated chromium hydroxide, a deep bluish-red syrup is obtained which will not crystallise, is completely soluble in alcohol and ether, and contains the constituents in the ratio $Cr_2O_3,3C_2O_3$. Neither the oxalic acid nor the chromium hydroxide can be detected by the ordinary methods. With chlorides of the alkaline earths, the compound gives beautifully crystalline salts containing chromium. With ammonia, no precipitate is obtained, and by prolonged boiling with excess of caustic alkali, a voluminous green precipitate is obtained. The *barium salt*, $Cr_2Ba_3(C_2O_4)_6,8H_2O$, crystallises in bright green needles having a red fluorescence, and has been previously obtained by Werner.

The *salts* of the composition $3R_2O,Cr_2O_3,6C_2O_3$, are obtained in a similar way to the preceding aluminium compounds, and are blue to bluish-red. The potassium salt crystallises with $6H_2O$ in monoclinic scales, the sodium salt with $9H_2O$ in tablets, and the ammonium salt with $6H_2O$ in leaflets.

The salts of the composition $2\frac{1}{2}R_2O,Cr_2O_3,5C_2O_3$ cannot be prepared. A green syrup containing the constituents in the right proportions is obtained in a similar manner to that described for the preparation of the aluminium compounds, but this syrup quickly decomposes with separation of chromium oxide, and then the preceding blue salts crystallise out. In one experiment, by cooling the green syrup to −20°, green needles were obtained, but they decomposed so rapidly that an analysis was not possible.

The salt, $2K_2O,Cr_2O_3,4C_2O_3,H_2O$, is obtained in a similar manner to the corresponding aluminium salt; it crystallises in deep green, microscopic needles. The sodium salt has also been obtained crystalline. The ammonium salt could not be obtained crystalline, but formed a gummy mass containing chromium oxide.

The salt, $K_2O,Cr_2O_3,4C_2O_3,10H_2O$, is obtained in a similar manner to the corresponding aluminium salt; it crystallises in beautiful deep red prisms.

III. *Alkali Ferric Oxalates.*—The author has examined the iron compounds obtained in a similar manner to the preceding. By the action of oxalic acid on freshly prepared ferric hydroxide, a deep yellow syrup is obtained, containing the constituents in the ratio $Fe_2O_3 : 3C_2O_3$. *Alkali iron oxalates* of the series 3 : 1 : 6 are obtained by saturating solutions of the acid alkali oxalates with ferric hydroxide. The salts of the composition $2\frac{1}{2}R_2O,Fe_2O_3,5C_2O_3$, like the preceding chromium compounds, cannot be obtained crystalline, although the analysis of the solution indicates their presence. The salts of the series 2 : 1 : 4 could not be prepared, and attempts to obtain them yielded green salts of the series 3 : 1 : 6, together with a brownish-red precipitate of variable composition containing all three constituents. The *salt* $K_2O,Fe_2O_3,4C_2O_3,5H_2O$, obtained in a similar manner to the aluminium salt, crystallises in bright brown crystals, and is decomposed when recrystallised, with formation of the green salt (3 : 1 : 6) and separation of ferric hydroxide.

The *salt*, $K_2O,Fe_2O_3,4MoO_3,2C_2O_3,10H_2O$, is obtained in beautiful bright yellow crystals by saturating a solution of the salt $3K_2O,Fe_2O_3,6C_2O_3,6H_2O$ with molybdic acid.

IV. Of the five types of compounds described, all the aluminium compounds, four of the chromium compounds, and three of the iron compounds are capable of existence, that is, the number of the complex acids varies with the basicity of the tervalent metal. The normal tribasic salts of the type $M'''(OOC{\cdot}COOR)_3$ are the most stable, and are easily obtained from the sesquioxides of iron, aluminium, and chromium, and also, though less easily, from the oxides of manganese and cobalt. By the addition of oxalic acid groups to the sesquioxides, acids are formed, which are stronger and more capable of forming salts according as more hydroxyl groups of the sesquioxide are replaced by oxalic acid groups, and also according to the less basic character of the sesquioxide.

E. C. R.

**Derivatives of Tartaric and Parapyruvic acids.** By EDUARD MULDER (*Rec. Trav. Chim.*, 1895, **14**, 281—306; compare Abstr., 1893, i, 685, and 1895, i, 449).—The author has continued his investigations on the products respectively soluble and insoluble in acetic acid, which result from the action of ethylic chloride on ethylic disodium tartrate.

On treatment with baryta water, a mixture of two substances was obtained. One of these, the crystalline barium compound, is shown to be barium oxalate, $BaC_2O_4 + 2H_2O$; it loses $1\frac{1}{2}H_2O$ at 120°, and the remaining $\frac{1}{2}H_2O$ at 120—140°. The other substance, the mamellated compound, when freed from barium oxalate, yields racemic acid, and a second crystalline acid, the constitution of which has not yet been determined. These three acids, oxalic, racemic, and the acid of unknown constitution, are regarded as decomposition products of tartryltartaric acid.

The author recommends slight modifications in the preparation of ethylic tartrates, and also in the manner of treatment of ethylic disodium tartrate with ethylic chloride.

Barium parapyruvate has the composition, $(C_3H_3O_3)_2Ba + H_2O$; parapyruvic acid itself is unstable, and readily loses carbonic anhydride and water.

J. J. S.

**Stereoisomeric Dimethyltricarballylic acids.** By NICOLAI D. ZELINSKY and N. TSCHERNOSWITOFF (*Ber.*, 1896, **29**, 333—339).—Ethylic cyanodimethylcarballylate, $COOEt{\cdot}C(CN)(CHMe{\cdot}COOEt)_2$ (compare Barthe, Abstr., 1888, 937, and *Ann. Chim. Phys.*, 1892, [6], **27**, 281), was prepared by the action of ethylic cyanacetate on ethylic $\alpha$-bromopropionate in the presence of sodium ethoxide, the fraction boiling at 190—210° (for the most part at 195—197°) being used for the further experiments. When heated with dilute sulphuric acid (1 : 1), it yields three acids, all of which have the composition, $C_8H_{12}O_6$, that is, $COOH{\cdot}CH(CHMe{\cdot}COOH)_2$; one of these is fairly insoluble in water, and melts at 203—204°; by fractional crystallisation of the mother liquor from this acid, the other two, melting respectively at 175—176° and 148—149°, were obtained. All three, when warmed with acetic chloride, yield crystallised isomeric anhydrides, $C_8H_{10}O_5$, melting respectively at 111—113°, 129—130°, and 117—119°, and these re-unite with water, reforming the original acids. But the acids also yield anhydrides, transparent, and viscid in character, when they are heated alone at 200—210°, and these, with water, regenerate the original acids, with the exception of the anhydride of the acid melting at 203—204°, which yields the acid melting at 148—149°. Further, the second and third acids are both transformed into the first (melting at 203—204°) when heated with hydrochloric acid at 190—200°. The isomerism of these three acids is, doubtless, of stereochemical nature.

C. F. B.

**Preparation of Amides and Acid Chlorides.** By ALBERT COLSON (*Compt. rend.*, 1895, **121**, 1155—1156).—When dry hydrogen chloride is passed into a mixture of a nitrile and an acid cooled at about 0°, an amide and an acid chloride are formed, $RCN + R'COOH + 2HCl = RCO{\cdot}NH_2,HCl + R'COCl$. Acetonitrile and acetic acid yield acetamide and acetic chloride; acetonitrile and propionic acid yield acetamide and propionic chloride; acetic acid and propionitrile yield propionamide and acetic chloride. Formic acid, under similar conditions, decomposes in a different manner. The well-known efficiency of hydrogen chloride in promoting the formation of ethereal salts is probably due to its tendency to convert acids into acid chlorides in presence of any substance which will combine with water.

Acid chlorides are formed still more easily if the acid in the above reaction is replaced by the anhydride. C. H. B.

**Method of Decomposition of some Amides and Imides.** By WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1895, **121**, 893—894).—The author has investigated the behaviour of various amides and imides with a solution of sodium hypochlorite, prepared by precipitating a solution of 50 parts of fresh bleaching powder in 500 parts of water, with a solution of 100 parts of sodium carbonate in 300 parts of water.

Formamide is decomposed slightly at the ordinary temperature, and more rapidly on heating. Acetamide is not decomposed, even when moderately heated. Propionamide begins to decompose in the cold, and the change becomes very rapid on heating; butyramide also decomposes on heating. Oxamide and succinamide behave like propionamide. Glycocine, amidopropionic acid (alanine), and asparagine decompose when gently heated; but hippuric acid is not decomposed unless strongly heated. Succinimide decomposes very rapidly, even at the ordinary temperature. In all cases the gas liberated has the negative properties of nitrogen. C. H. B.

**New Salts of Amides.** By J. TOPIN (*Ann. Chim. Phys.*, [7], **5**, 99—132).—*Basic acetamide hydrobromide*, $(C_2H_5NO)_2,HBr$, is obtained when a solution of acetamide in equal parts of alcohol and ether is treated with pure, dry, gaseous hydrogen bromide. It is necessary to pass the gas in a slow stream, and to keep the vessel containing the solution of acetamide cool by means of cold water. The hydrobromide crystallises in colourless, odourless, fragile needles, which have an acid taste and reaction. It melts at 139·5°, and shortly afterwards decomposes, is readily soluble in water, sparingly in alcohol, and insoluble in ether, and is decomposed by alkalis.

The author was not able to prepare acetamide hydriodide.

*Acetamide platinochloride*, $(C_2H_5NO)_2,H_2PtCl_6$, obtained from aqueous solutions of acetamide and platinic chloride, is an orange-yellow crystalline powder, which is very sparingly soluble in water, even less so in alcohol, and melts and decomposes at 225°.

*Acetamide hydrogen oxalate*, $C_2H_5NO,2C_2H_2O_4$, is best obtained by adding acetamide (1 mol.) in concentrated aqueous solution to oxalic acid (2 mols.), also in aqueous solution; it is also formed when the two compounds, in molecular proportion, are mixed in aqueous or alcoholic solution. It crystallises in colourless prisms or plates, and melts at 129°.

Another *oxalate*, $C_2H_5NO,C_2H_2O_4$, was obtained by the author on adding the amide (2 mols.) to oxalic acid (1 mol.); it forms small, colourless, brilliant prisms, which are readily soluble in water and in alcohol, and redden blue litmus.

The *acid tartrate*, $C_2H_5NO,C_4H_6O_6$, is best obtained by treating acetamide in alcoholic solution with an excess of tartaric acid. It crystallises in colourless plates, melts at 130·5°, is extremely soluble in water, more sparingly in alcohol, and has an acid reaction. It is decomposed on heating, and also, like all the other salts of amides, on treatment with alkalis.

The *normal tartrate*, $(C_2H_5NO)_2,C_4H_6O_6$, is obtained when 2 mols. of the amide are taken for each molecule of acid. It forms short, brilliant crystals, with small facets; on heating, it turns brown at 190°, and decomposes at about 225°.

*Acetamide picrate*, $C_2H_5NO,C_6H_3N_3O_7$, may easily be prepared by the action of picric acid on acetamide in alcoholic solution, or by dissolving the amide in fused picric acid. The salt is moderately soluble in alcohol, somewhat more sparingly in water. When carefully heated, it melts at 117·5°. It crystallises in small prisms, of a brilliant yellow colour.

*Normal oxamide tartrate*, $(C_2H_4N_2O_2)_2,C_4H_6O_6$, crystallises in small, orthorhombic plates; it dissolves readily in water, more sparingly in alcohol; it has acid properties, and in aqueous solution is dextrorotatory, practically to the same extent as the normal acetamide tartrate (compare Wyrouboff, Abstr., 1894, ii, 177).

*Basic acetanilide hydrobromide*, $2C_8H_9NO,HBr$, may be prepared in much the same way as the acetamide hydrobromide. It crystallises in small, colourless needles, which are readily soluble in water and in alcohol, but almost insoluble in ether.

*Acetanilide platinochloride*, $(C_8H_9NO)_2,H_2PtCl_6$, crystallises in orange-yellow needles, which are only very sparingly soluble in water and in alcohol.

*Acetanilide picrate*, $C_8H_9NO,C_6H_3N_3O_7$, crystallises in yellow prisms. It is but sparingly soluble in water and in alcohol, and decomposes when gently heated.

The crystallographic properties of most of the salts are given in detail. J. J. S.

**Synthesis of Complex Amides.** By ALBERT COLSON (*Compt. rend.*, 1895, **121**, 825—827).—*Cyanoisobutaldehyde acetate*,

$$OAc·CH(CN)·CHMe_2,$$

is a stable compound which boils, without decomposing, at 189° under ordinary pressure, and is insoluble in water (compare Abstr., 1895, ii, 257).

*Acetyllactylacetamide*, NHAc·CO·CHMe·OAc, constitutes the fraction which boils at about 178°, when the product of the action of acetic chloride on the lactic nitrile (*loc. cit.*) is distilled under a pressure of 15 mm. It forms white, hygroscopic crystals which, when dry, melt at 73°. When dissolved in warm water, it forms a crystalline hydrate containing 1 mol. $H_2O$. It has none of the properties of cyanides, and yields no ammonia with aqueous potash in the cold. When heated in sealed tubes with water at 150°, it splits up into ammonium acetate and acetic and lactic acids.

*Diacetyldilactamide*, $NH(CO{\cdot}CHMe{\cdot}OAc)_2$, is obtained by the action of water at 0° on the crystalline product, $OAc{\cdot}CHMe{\cdot}CN + HCl$, obtained by the action of dry hydrogen chloride on cooled cyanisobutaldehyde acetate. It forms white, nacreous needles which melt at 110°, and, when heated with water at 150°, yields 3 mols. of acid. When dissolved in benzene, it forms crystals of the compound $NH(C_5H_7O_3)_2 + C_6H_6$, but when dissolved in acetic acid, its molecular weight is found to be 230 (calc. 245).

The formation of these amides is probably analogous to that of amides from nitriles by the action of water; the change is determined by the presence of a small quantity of hydrochloric acid, and takes place according to the equation, $R{\cdot}CN + Ac{\cdot}OH = R{\cdot}CO{\cdot}NHAc$. C. H. B.

**Biuret Reactions.** By HUGO SCHIFF (*Ber.*, 1896, **29**, 298—303).—Biuret is best prepared by heating the liquid carbamide hydrochloride at 130°, and then separating the biuret from the potassium cyanate which is formed on treating the product with weak alcoholic potash. The following metallic derivatives have been examined and analysed. The *potash compound*, $C_2H_5N_3O_2,KOH$, crystallises in needles, and is decomposed by water and by the carbonic anhydride of the air. The compound with soda, $C_2H_5N_3O_2,NaOH$, has similar properties. Mercuric oxide forms two compounds,

$$C_2H_5N_3O_2,HgO \text{ and } Hg(C_2H_4N_3O_2)_2,2HgO,$$

both of which are obtained by adding mercuric nitrate to an aqueous solution of biuret.

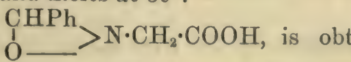
Biuret unites with the soluble copper salts, forming light blue, crystalline compounds such as $CuSO_4,2C_2H_5N_3O_2$, $CuCl_2,2C_2H_5N_3O_2$, which are partially decomposed by water. The violet compound formed in the well known biuret reaction is best prepared by adding copper acetate solution to biuret, and then precipitating with alcoholic potash. It forms long, carmine-red needles, which may be preserved under weak alcoholic potash; this compound has the composition $2C_2H_5N_3O_2,2KOH,Cu(OH)_2$, the metals being probably united with the nitrogen of the amido-groups. Nickel salts behave towards biuret in the same manner as the copper salts, pale green compounds being produced, which form yellow solutions in aqueous potash. Cobalt salts also combine with biuret, but the products do not give a characteristic coloration with potash. The biuret reaction with potash and a copper or nickel salt, appears to be given by all such diamides as contain two $-CO{\cdot}NH_2$ groups united together, or with a single atom of carbon or nitrogen, or with several $-CO{\cdot}NH$ groups in an open chain. Thus malonamide and oxalyldiureïde, $NH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, give the reaction, whilst succinamide does not. A. H.

**Oximes of α-Halogenised Aldehydes, Ketones, and Acids: Oximido-acetic acids.** By ARTHUR R. HANTZSCH and WILHELM WILD (*Annalen*, 1896, **289**, 285—309).—The authors have found that hydroxylamine converts α-halogenised aldehydes and α-halogenised ketones of the type $R\cdot CHX\cdot CO\cdot R'$ into glyoximes of the general formula $R\cdot C(NOH)\cdot C(NOH)R'$, whilst α-halogenised acids yield α-oximido-acids of the type $R\cdot C(NOH)\cdot COOH$. Thus methylglyoxime has been obtained by the action of hydroxylamine on chloracetone, whilst dichlorethylic ether and amidothiazole have given rise to glyoxime; mono- and di-chloracetic acids yield oximidoacetic acid, whilst α-oximidopropionic and α-oximidobutyric acids are obtained from α-bromopropionic and α-bromobutyric acid respectively.

*Oximidoacetic-acetic acid*, $COOH\cdot CH:N\cdot O\cdot CH_2\cdot COOH$ ("oximido-essigacetsäure"), is produced along with oximidoacetic acid when hydroxylamine acts on chloracetic acid; it crystallises from water in needles, and melts at 181°, yielding hydrogen cyanide. This acid is indifferent towards acetic anhydride and acetic chloride, but phosphorus pentachloride converts it into the oily *chloride;* neither ammoniacal silver nor Fehling's solution is reduced by the acid when boiled with it. The *ammonium* salt is a crystalline precipitate, and the *barium* salt, containing $1H_2O$, separates in small needles; the *silver* salt is crystalline, and the *amide* crystallises in leaflets and melts and decomposes at 214°. When the acid is reduced with hydriodic acid, glycocine is produced, and hot alkalis give rise to carbonic anhydride, hydrogen cyanide, and glycollic acid; it is indifferent towards boiling mineral acids, but at 140°, it is decomposed by 35 per cent. sulphuric acid into carbonic anhydride, ammonia, formic acid, and glycollic acid.

*Oximidopropionic-acetic acid* (compare Wolff, this vol., i, 88), $COOH\cdot CMe:N\cdot O\cdot CH_2\cdot COOH$, is obtained by heating oximidopropionic and chloracetic acids with aqueous potash at 50—60° for three hours; it melts and decomposes at 130—132°. The acid is indifferent towards ammoniacal silver and Fehling's solution, and is not attacked by boiling alkalis and concentrated hydrochloric acid; the *silver* salt crystallises from hot water, and coloured precipitates are formed with copper and lead acetates, and ferric chloride. Amidopropionic acid is obtained on reducing the acid with hydriodic acid.

*Normal benzaldoximido-acetic acid*, $CHPh:N\cdot O\cdot CH_2\cdot COOH$, is obtained by heating molecular proportions of the potassium derivative of benz-antialdoxime and potassium chloracetate in aqueous solution; it crystallises from hot water in long needles, and melts at 98°. It is indifferent towards Fehling's solution and boiling concentrated hydrochloric acid; alkalis convert it into benzonitrile and glycollic acid, whilst hydriodic acid at 100° gives rise to benzaldehyde, ammonia, and glycollic acid. The *potassium* salt contains $1H_2O$, and crystallises from water, whilst the *tin* salt separates in long needles; the *ethylic* salt crystallises in long needles, and melts at 59°.

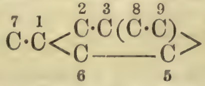
*Isobenzaldoximido-acetic acid*,  $\left.\begin{matrix}CHPh\\ | \\ O\end{matrix}\right>N\cdot CH_2\cdot COOH$, is obtained from benzsynaldoxime and chloracetic acid; it crystallises in long needles, and melts at 183°, decomposing vigorously at this temperature.

Reduction with hydriodic acid gives rise to benzaldehyde and glycocine; it is readily oxidised by ferric chloride and Fehling's solution, yielding benzaldehyde, which is also formed under the influence of caustic potash and boiling hydrochloric acid.

Hydroxylamidoacetic acid (Traube, this vol., i, 9) is obtained along with benzaldehyde when isobenzaldoximidoacetic acid is treated with boiling hydrochloric acid. M. O. F.

**Action of Hydroxylamine on Ethylic Succinate.** By GIORGIO ERRERA (*Gazzetta*, 1895, **25**, ii, 263—266).—By the action of hydroxylamine on ethylic succinate, Hantzsch and Urbahn (Abstr., 1895, i, 393) were unable to prepare pure succinylhydroxamic acid, but got a product which, on acetylation, yielded what they supposed to be a tetracetylsuccinylhydroxamic acid; this, however, the author finds to be the succinylacetoxylamine which he has recently described (this vol., i, 209). The behaviour of ethylic succinate towards hydroxylamine is, therefore, exactly similar to that of methylic phthalate (this vol., i, 222). W. J. P.

**Synthesis in the Pentamethylene Series.** By NICOLAI D. ZELINSKY and M. RUDSKY (*Ber.*, 1896, **29**, 403—405).—Dimethyladipic acid, when distilled with calcium hydroxide, yields *dimethylketopentamethylene*; this boils at 145—147°, and does not combine with sodium hydrogen sulphite. The yield is 32 per cent. of the acid employed. When reduced by means of sodium in moist ethereal solution, a corresponding *alcohol* is formed; it boils at 154° (744 mm.), and has a sp. gr. = 0·9224 0°/0°. The yield is 75 per cent. of the ketone. By the action of hydriodic acid (sp. gr. = 1·96) at 100°, an oily *iodide* is formed, and this, by the further action of hydriodic acid at 220°, is converted into 1 : 3-*dimethylpentamethylene* boiling at 93° (743 mm.), the sp. gr. = 0·7543 at 20°/4°, the refractive index $n$ = 1·4130 at 20°, and the molecular refractive power = 32·38, which agrees with the theoretical value for a saturated hydrocarbon. The compound has an odour of petroleum, is immediately coloured by bromine vapour, and quickly dissolves in fuming (yellow) nitric acid; this readily distinguishes it from the synthetical hexamethylene hydrocarbons which, at the ordinary temperature, are extremely stable towards nitric acid either alone or with sulphuric acid. J. B. T.

**Syntheses in the Camphor and Terpene Series.** By EMIL KNOEVENAGEL (*Annalen*, 1895, **289**, 131—172; compare Abstr., 1895, i, 48, also Baeyer, Abstr., 1893, i, 258).—The author has synthesised numerous meta-alkyl derivatives of hydrogenised toluene by reducing certain cycloïd ketones which have been already described (*loc. cit.*); elimination of water from the phenols obtained in this way has given rise to dihydrotoluene derivatives. The carbon atoms are numbered as indicated by the expression  $\overset{7}{C}\cdot\overset{1}{C}<\begin{matrix}\overset{2}{C}\cdot\overset{3}{C}(\overset{8}{C}\cdot\overset{9}{C})\\ \underset{6}{C}\text{———}\underset{5}{C}\end{matrix}>\overset{4}{C}$, and reference is made to $\Delta_2$-ketotetrahydrobenzene derivatives as cyclohexenones.

*Tetrahydrometacresol* (*methyl*-1-*cyclohexenol*-5) is obtained by reducing methyl-1-cyclohexenone-5 with sodium and alcohol; it is a colourless, viscous oil, which boils at 175—176°, and is volatile in alcohol vapour and in steam. The sp. gr. = 0·9320 at 15°, and the refractive index $n_D$ = 1·4695 at 15°, whence the molecular refraction R = 33·48. The substance is unsaturated, and gives rise to a liquid dibromide. The *acetyl* derivative boils at 188—189°, and the *urethane*, $C_{14}H_{17}O_2N$, obtained from phenylic isocyanate, melts at 90°; the *chloride* is obtained by the action of phosphorus pentachloride, and decomposes slightly when boiled in a vacuum.

*Tetrahydro*-1 : 3 : 5-*xylenol* (*dimethyl*-1 : 3-*cyclohexenol*-5) is obtained from dimethyl-1 : 3-cyclohexenone-5, and boils at 187° under atmospheric pressure, and at 83° under a pressure of 15 mm.; the sp. gr. = 0·9056 at 15° and 0·9007 at 20·5°. The refractive index $n_D$ = 1·4539 at 20·5°, whence the molecular refraction R = 37·88. The *dibromide* crystallises in colourless needles, and melts at 148°; the *acetyl* derivative is a limpid, colourless liquid, which boils at 195—196°. The *urethane* melts at 107°, and the *chloride* is a highly refractive oil, which boils at 80—85° under a pressure of 25 mm.; the *bromide* becomes brown and resinous in air, and the *iodide* boils at 110—115° under a pressure of 25 mm.

*Tetrahydro*-1 : 3 : 5-*carvacrol* (*methyl*-1-*isopropyl*-3-*cyclohexenol*-5) is a colourless, viscous oil having the odour of peppermint; it boils at 112°, 125°, and 150° under pressures of 14 mm., 22 mm., and 65 mm. respectively, and under atmospheric pressure, it boils at 224°. The sp. gr. = 0·9090 at 15°, and the refractive index $n_D$ = 1·4684 at 15°, whence the molecular refraction R = 47·02. The *acetyl* derivative is a colourless liquid having an agreeable odour, and boils at 228°; the *methyl ether* boils at 122° under a pressure of 40 mm. The *chloride*, $C_{10}H_{17}Cl$, obtained from tetrahydrocarvacrol by the action of phosphorus pentachloride, is a colourless, highly refractive oil, which boils at 99—100° under a pressure of 22 mm.; the *bromide* boils at 158° under a pressure of 24 mm.

*Meta-isobutyltetrahydrometacresol* (*methyl*-1-*isobutyl*-3-*cyclohexenol*-5) is obtained by reducing methyl-1-isobutyl-3-cyclohexenone-5 with sodium and alcohol; it boils at 119° and 127—129° under pressures of 10 mm. and 20 mm. respectively. At 21·5°, the sp. gr. = 0·8909, and the refractive index $n_D$ = 1·4614, whence the molecular refraction R = 51·77. The *acetyl* derivative boils at 132—134° under a pressure of 18 mm., and the *methyl ether* at 112° under a pressure of 9 mm.; the *isopropyl ether* boils at 116° under a pressure of 10 mm.

*Metahexyltetrahydrometacresol* (*methyl*-1-*hexyl*-3-*cyclohexenol*-5) boils at 147—149° under a pressure of 20 mm., and has the sp. gr. = 0·8840 at 21·5°, and the refractive index $n_D$ = 1·4617 at 21·5°, whence the molecular refraction R = 60·92. The *acetyl* derivative boils at 154—156° under a pressure of 22 mm., and the *methyl ether* at 135—136° under a pressure of 10 mm.; the *isopropyl ether* has a disagreeable odour, and boils at 138—139° under a pressure of 10 mm.

When the bromide of tetrahydrometacresol is distilled with 10 parts of quinoline, dihydrotoluene is produced (compare Baeyer, *Annalen*, **155**, 271), and it is also obtained by treating tetrahydrometacresol vith phosphoric anhydride. It boils at 106—107°, and has sp. gr. = 0·8088 at 15°, and 0·8017 at 18·3°, and the refractive index $n_D$ = 1·4460 at 18·3°, whence the molecular refraction R = 31·20.

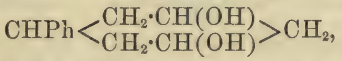
*Dihydrometaxylene* is obtained from tetrahydro-1 : 3 : 5-xylenol by the action of phosphoric anhydride and by distilling the bromide with quinoline; it is also produced when the hydrochloride of tetrahydro-xylidine (Abstr., 1895, i, 52) is subjected to dry distillation, and by reducing symmetrical chlorodihydro-xylene (*loc. cit.*, 86). Dihydrometaxylene is a limpid, colourless liquid, which boils at 123°; at 15° and 20·5° the sp. gr. = 0·7988 and 0·7948 respectively, whilst the refractive index $n_D$ = 1·4416 at 20·5°, and therefore the molecular refraction R = 35·92. Alcoholic sulphuric acid (4 parts of alcohol and 1 of acid) develops a reddish-violet coloration, which subsequently becomes blue; when half the proportion of alcohol is employed, the liquid acquires a yellow tint, which changes to reddish-yellow, and finally becomes blue. These phenomena are attended with marked changes in the absorption spectra. Wallach has obtained a ketone isomeric with dimethyl-1 : 3-cyclohexenone-5, which yields dihydrometaxylene under the influence of zinc chloride (*Annalen*, **258**, 327), but the substance boils at 132—134°; both hydrocarbons, however, are converted into trinitrometaxylene (m. p. 180—181°) on nitration.

*Dihydrometacymene* (*methyl*-1-*isopropyl*-3-*cyclohexadiene*) is obtained by eliminating hydrogen bromide from the bromide of tetrahydro-1 : 3 : 5-carvacrol, or, more conveniently, by dehydrating this substance with phosphoric anhydride at 120°; it boils at 171—172°, and has an odour recalling that of benzene, but like that of oranges, when diluted. The sp. gr. = 0·8170 at 15·5°, and the refractive index $n_D$ = 1·4564 at 15·5°, whence the molecular refraction R = 45·29. The hydrocarbon reduces a cold solution of potassium permanganate, and takes up four atomic proportions of bromine. Alcoholic sulphuric acid (4 parts of alcohol and 1 of acid) develops a wine-red coloration with dihydrometacymene, gradually becoming violet-red; one-half the proportion of alcohol gives rise to a yellow tint, which becomes reddish-yellow, and subsequently violet, whilst the coloured liquids exhibit characteristic absorption spectra. The *nitrosochloride* of dihydrometacymene melts at 150°. Repeated treatment of dihydrometacymene with bromine and quinoline has given rise to metacymene, identical with the hydrocarbon obtained by Wallach from fenchone (Abstr., 1895, i, 380); metacymene, from both sources, yields a yellow *trinitro*-derivative, which melts at 72°.

*Meta-isobutyldihydrotoluene* (*methyl*-1-*isobutyl*-3-*cyclohexadiene*) is obtained from meta-isobutyltetrahydrometacresol by the action of phosphoric anhydride; it is a limpid, colourless liquid, which boils at 185°. The sp. gr. = 0·8089 at 21·5°, and the refractive index $n_D$ = 1·4501 at 21·5°, whence the molecular refraction R = 49·83; characteristic colorations and absorption spectra are developed with alcohol and sulphuric acid. The hydrocarbon takes up four atomic proportions of bromine, but the product spontaneously loses hydrogen bromide, and, when treated with quinoline, yields an oil, which probably contains meta-isobutyltoluene, because nitration gives rise to 2 : 4 : 6-*trinitroisobutyltoluene*, which has the odour of musk, and is isomeric with Baur's "artificial musk;" this compound, which crystallises from alcohol and melts at 124°, is also obtained from isobutyldihydrotoluene.

*Metahexyldihydrotoluene* (*methyl*-1-*hexyl*-3-*cyclohexadiene*) is produced when phosphoric anhydride acts on metahexyltetrahydrometacresol at 165°; it boils at 228—230°, has the sp. gr. = 0·8216 at 21·5°, and the refractive index $n_D = 1{\cdot}4562$ at 21·5°, whence the molecular refraction R = 58·90. The hydrocarbon takes up four atomic proportions of bromine, and, on treating the product with quinoline, an oil containing metahexyltoluene is obtained; on nitration, this yields 2 : 4 : 6-*trinitrometahexyltoluene*, which melts at 131°, and has a feeble odour of musk.

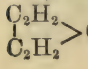
*Metaphenylhexahydroresorcinol* (*phenyl*-5-*cyclohexanediol*-1 : 3),



$$\mathrm{CHPh}<\begin{matrix}\mathrm{CH_2{\cdot}CH(OH)}\\ \mathrm{CH_2{\cdot}CH(OH)}\end{matrix}>\mathrm{CH_2},$$

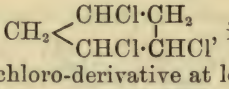
is obtained by reducing phenyldihydroresorcinol with alcohol and sodium; it crystallises from water in lustrous leaflets, and melts at 157°. It is insoluble in benzene, and sparingly soluble in chloroform and ether; it does not dissolve more readily in potash than in water, and crystallises unaltered from the solution. When heated with phosphoric anhydride, it yields *dihydrodiphenyl*, which melts at 66—66·5°, and, although extremely soluble in alcohol and ether, crystallises well from these solvents; it is volatile in steam, and reduces a warm solution of potassium permanganate.

Diethylic 5-methyl-1 : 3-diketocyclohexane-4 : 6-dicarboxylate (Abstr., 1894, i, 577) is obtained from ethylic ethylidenemalonate and ethylic acetoacetate under the influence of sodium ethoxide. Hydrolysis and elimination of carbonic anhydride converts it into *metamethyldihydroresorcinol*, which crystallises from water, and melts at 125—126°; the aqueous solution is acidic, decomposing carbonates, develops a red coloration with ferric chloride, and reduces potassium permanganate. Metamethyldihydroresorcinol is a homologue of Merling's dihydroresorcinol (Abstr., 1894, i, 177), and, like that substance, yields a *compound* with formaldehyde; this crystallises from alcohol in lustrous needles, and melts at 152—153°. The *dioxime* of metamethyldihydroresorcinol melts at 155°. M. O. F.

**The Cyclopentadiene of Coal Tar; the Indene of the Aliphatic Series.** By GUSTAV KRAEMER and ADOLF SPILKER (*Ber.*, 1896, **29**, 552—561).—The hydrocarbon of the formula $C_5H_6$, which the authors obtained from coal tar (Abstr., 1891, 205), and to which Étard and Lambert, having isolated the substance from the condensation products of oil gas, have given the name pyropentylene (Abstr., 1891, 1085), has been submitted to further investigation; it is identical with the hydrocarbon described by Roscoe (Trans., 1885, **47**, 669), and, as the constitution is probably represented by the formula  $\begin{matrix}\mathrm{C_2H_2}\\ |\\ \mathrm{C_2H_2}\end{matrix}>\mathrm{CH_2}$, the authors refer to it as the cyclopentadiene of coal tar.

The hydrocarbon boils at 41° (corr.) under a pressure of 760 mm., and has the sp. gr. = 0·80475 at 18·6°/4°; it becomes resinous under the influence of alkalis and dilute acids, and is charred by concentrated sulphuric acid, the action of fuming nitric acid being so vigorous as to cause ignition. The refractive index $n_D = 1{\cdot}4446$ at 18·6°, whence the molecular refraction $M = 36{\cdot}45$, the value calculated for two ethylene linkings being $M = 36{\cdot}04$.

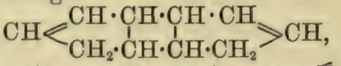
*Chlorocyclopentene*, $C_5H_7Cl$, is obtained by saturating a solution of cyclopentadiene in chloroform, at low temperatures, with hydrogen chloride; it boils at 50° under a pressure of 40 mm., and has the sp. gr. = 1·0571 at 15°/15°. It becomes resinous spontaneously, and loses hydrogen chloride; aqueous ammonia converts it into a substance resembling india-rubber, an unsaturated alcohol, and an unsaturated *base*, $C_5H_7NH_2$, which boils at 102—104°, and forms a *platinochloride*.

*Trichlorocyclopentane*,  $\mathrm{CH_2}{<}\begin{array}{l}\mathrm{CHCl\cdot CH_2}\\ \mathrm{CHCl\cdot CHCl}\end{array}$, is produced by the action of chlorine on the monochloro-derivative at low temperatures; it boils at 195—197°, and has the sp. gr. = 1·3695 at 20°/4°. The substance is indifferent towards cold, concentrated sulphuric and fuming nitric acids, and is slowly attacked by bases.

*Tetrachlorocyclopentane*, $C_5H_6Cl_4$, is obtained by leading chlorine into a solution of cyclopentadiene in chloroform at −15°; it boils at 94° and 103° under pressures of 15 mm. and 25 mm. respectively, and has the sp. gr. = 1·423 at 15°.

*Dibromocyclopentene*, $C_5H_6Br_2$, is produced when bromine combines with cyclopentadiene at temperatures approaching − 20°; it crystallises in colourless prisms, and melts at 45—46°. The substance decomposes spontaneously, and is attacked vigorously by bases and concentrated acids.

*Tetrabromocyclopentane*, $C_5H_6Br_4$, is obtained from the foregoing compound by the action of bromine; it is a pale yellow liquid, having a sp. gr. = 2·5224 at 15°/4°, and distils under diminished pressure without undergoing change.

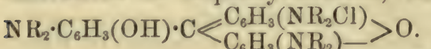
*Dicyclopentadiene*,  $\mathrm{CH}{<}\begin{array}{l}\mathrm{CH\cdot CH\cdot CH\cdot CH}\\ \mathrm{CH_2\cdot CH\cdot CH\cdot CH_2}\end{array}{>}\mathrm{CH}$, is formed from cyclopentadiene by spontaneous change (compare Étard and Lambert; also Roscoe). It solidifies at 32·5°, and has the sp. gr. = 0·9766 at 33°/4°; under pressures of 35 mm., 55 mm., and 760 mm., it boils at 88°, 95°, and 170° respectively, being in part converted into cyclopentadiene at the last named temperature. The refractive index $n_D = 1{\cdot}5050$ at 35°, whence the molecular refraction $M = 68{\cdot}44$, the calculated value being $M = 68{\cdot}1$. The *nitrosochloride* melts at 182°, and is converted by piperidine into a *base*, which melts at 160°; the *nitrosate* crystallises in lustrous prisms, and melts at 155°. Dicyclopentadiene forms additive compounds with halogens, but the derivatives are unstable; it immediately reduces a cold solution of potassium permanganate. M. O. F.

**Derivatives of Metaxylene.** By A. Klages (*Ber.*, 1896, **29**, 310—314).—Symmetrical chloroxylene may be prepared from symmetrical xylidine by means of Sandmeyer's reaction; the product is identical with that previously obtained by Klages and Knoevenagel (Abstr., 1895, i, 86) from dimethylketotetrahydrobenzene. 5-*Chlorometaxylene-2-sulphonic acid* forms colourless crystals melting at 52°, and is not hygroscopic. When fused with potash, it yields metaxyloquinol melting at 149—150°. The sulphonic acid is accompanied by a small amount of its anhydride. The *sulphonic chloride* forms large, rhombic crystals, and melts at 56—58°, whilst the *amide* crystallises in colourless needles, and melts at 191—192°. Symmetrical chloroxylene is converted by fuming nitric acid and sulphuric acid into the 2 : 4 : 6-*trinitro-compound*, which melts at 218°. 4-*Chloro-5-nitrometaxylene* is prepared from 5-nitro-1 : 3 : 4-xylidine by Sandmeyer's reaction. It boils at 278°, melts at 52°, and, when reduced, yields 4-*chloro*-1 : 3 : 5-*xylidine*, which boils at 251°, and combines with the carbonic anhydride of the air; its *benzoyl derivative* melts at 128°. This base is usually accompanied by a *dichloro*-1 : 3 : 5-*xylidine*, which crystallises in colourless needles, melts at 72°, boils at 265—266°, and yields a *benzoyl derivative*, which melts at 158°. 4 : 5-*Dichlorometaxylene* can readily be obtained from 4-chloro-1 : 3 : 5-xylidine by means of Sandmeyer's reaction, and boils at 231—232°. 2 : 5-*Dinitro*-1 : 3 : 4-*aceto-xylidide* forms almost colourless needles melting at 226°, and dissolves in warm aqueous potash, forming an unstable potassium compound. 2 : 5-*Dinitro*-1 : 3 : 4-*xylidine* crystallises in yellow needles melting at 115°, which deflagrate when heated. This base can only be converted into the corresponding hydrocarbon with great difficulty. The resulting 2 : 5-dinitrometaxylene melts at 132°, and, when reduced, yields a base, the *benzoyl derivative* of which melts at 234°. 4-*Chloro*-2 : 5-*dinitrometaxylene*, obtained by means of Sandmeyer's reaction, forms yellow crystals, melts at 61°, and boils at 290—291°. On reduction, it yields the corresponding *base*, which boils at 280—281° and forms a *benzoyl derivative* melting at 164°. This base is readily converted, by treatment with ferric chloride and hydrochloric acid, into 4-*chlorometaxyloquinone*, which crystallises in compact needles melting at 218°. The formation of this substance proves that the base from which it is obtained, and the corresponding dinitro-compound, have the constitutions which have been assigned to them above. A. H.

**Phenylic Ethers of Nitro-compounds of Iron.** By KARL A. HOFMANN and O. FRITZ WIEDE (*Zeit. anorg. Chem.*, 1896, **11**, 288—292; see also Abstr., 1895, ii, 451).—Dinitrosoferrophenyl mercaptide, $Fe(NO)_2SPh$, which can only be obtained with difficulty by the method previously described, is easily prepared by adding the theoretical quantity of phenylhydrazine (7 mols.) to an alcoholic solution of potassium heptanitrosoferrothiosulphonic acid, $Fe_4(NO)_7S_3K,H_2O$; the mixture being well cooled with ice, and allowed to remain two days. It crystallises in brown, lustrous plates, and melts at 179°. It is also obtained on gradually adding the theoretical quantity of diazobenzene nitrate to a solution of potassium heptanitrosoferrothiosulphonic acid in absolute alcohol, and cooling with ice. A determination of the molecular weight by the cryoscopic method gave numbers agreeing with the formula $[Fe(NO)_2SPh]_2$. E. C. R.

**Action of Carbonyl Chloride on Dimethyl- and Diethylmetamidophenol.** By FRIEDRICH VON MEYENBURG (*Ber.*, 1896, **29**, 501—513).—Carbonyl chloride reacts with dimethyl- and diethylmetamidophenol in the cold to form ethereal salts of carbonic and chloro-formic acids. At higher temperatures, red and violet colouring matters are produced. *Metadimethylamidophenylic carbonate*, $CO(O\cdot C_6H_4\cdot NMe_2)_2$, is formed when an alkaline solution of metadimethylamidophenol is shaken with a solution of carbonyl chloride in benzene. It crystallises in long, feathery needles, melts at 137—138°, and boils at 265° (pressure = 15 mm.). It dissolves in moderately strong acids, but is insoluble in alkalis and water; it is not affected by aqueous potash at 100°, but is hydrolysed by alcoholic potash, &c. The salts are unstable, and readily lose a portion of their acid; the *hydrochloride* crystallises in flat needles, and melts and decomposes at 205°; the *picrate* melts at 162°, whilst the *platinochloride* forms golden-yellow granules, and is very unstable. *Metadimethylamidophenylic chloroformate*, $COCl\cdot O\cdot C_6H_4\cdot NMe_2$, is formed when dimethylamidophenol in benzene solution is added to an excess of carbonyl chloride dissolved in the same solvent. It is obtained as a syrup, which decomposes when preserved, and has not been analysed. Water decomposes it with evolution of carbonic anhydride.

*Metadiethylamidophenylic carbonate* crystallises in colourless prisms melting at 67°, and boils at 292° (pressure = 5 mm.). The salts are less stable than those of the dimethyl compound. The *hydrochloride* melts and decomposes at 205°, and the *hydriodide* melts at 201°. *Metadiethylamidophenylic chloroformate*, forms a syrup which partially solidifies when preserved at 0° for some days. *Metadiethylamidophenylic acetate* is a colourless oil which boils at 160·5° (pressure = 5 mm.).

When the dialkylamidophenols are heated with carbonyl chloride at 160°, red colouring matters are formed, which are probably derivatives of triphenylmethane, and have the general formula  $NR_2\cdot C_6H_3(OH)\cdot C{<}\begin{matrix}C_6H_3(NR_2Cl)\\ C_6H_3(NR_2)-\end{matrix}{>}O$. These substances closely resemble the pyronines in colour and absorption spectrum, and the author proposes to call them *phosgenepyronines*. The red colouring matter from diethylamidophenol forms a violet *sodium salt*, the solution of which is decolorised on heating, the red colouring matter being precipitated. The base of the colouring matter appears to exist in two forms, for when the violet solution of the sodium salt is shaken with toluene, a violet solution is obtained, whereas the base precipitated by boiling from the alkaline solution dissolves in toluene, forming a reddish-yellow solution. Both solutions yield the original colouring matter when extracted with dilute acid. When the dialkylamidophenols are heated with carbonyl chloride at 100°, violet colouring matters are formed, the colour bases of which also appear to exist in two forms. These substances could not be analysed.

A. H.

**Derivatives of Isanethoil.** By Carl Hell and Carl Gaab (*Ber.*, 1896, **29**, 344—352).—Isanethoil, $OMe\cdot C_6H_4\cdot CH_2\cdot CH{:}CH_2$, was obtained by fractionating essence of tarragon, and formed the chief constituent of the fraction boiling at 208—214°, which was about one-half of the whole. It was brominated in cooled ethereal solution, when a compound, $OMe\cdot C_6H_3Br\cdot CH_2\cdot CHBr\cdot CH_2Br$, melting at 62·4°, was obtained; it was not found possible to add bromine without substitution occurring at the same time, nor was it possible to introduce more than 1 bromine atom into the $C_6H_4$ group. When this bromine derivative is oxidised with chromic acid in acetic acid solution, it yields a *tribromo-ketone*, $OMe\cdot C_6H_3Br\cdot CO\cdot CHBr\cdot CH_2Br$, melting at 103·5°; whereas the isomeric bromide from anethoïl,

$$OMe\cdot C_6H_3Br\cdot CHBr\cdot CHBr\cdot CH_3,$$

yields only a dibromo-ketone, which must have the formula

$$OMe\cdot C_6H_3Br\cdot CO\cdot CHBr\cdot CH_3,$$

for had it been the other CHBr-group that underwent oxidation, there would be no reason why the same CHBr-group should not undergo oxidation in the case of the iso-compound. It would seem therefore that it is always the group next to the benzene ring which is oxidised, the position of the bromine atoms being without influence.

This ketone is oxidised by permanganate to bromanisic acid; no acetic acid is formed. With alcoholic ammonia at 110°, it forms a compound, apparently of the composition

$$[OMe\cdot C_6H_3Br\cdot CO\cdot CH(NH_2)\cdot CH_2]_2NH.$$

With alcoholic potassium acetate, it yields a compound, possibly $OMe\cdot C_6H_3Br\cdot CO\cdot CH(OAc)\cdot CH_2\cdot OAc$. With sodium ethoxide, it does not yield an ethoxy-derivative; bromanisic acid is formed. These last experiments were performed with very small quantities of substance, and great importance cannot be attached to the results.

C. F. B.

**Constitution of Phenoquinone.** By C. Loring Jackson and George Oenslager (*Amer. Chem. J.*, 1896, **18**, 1—22).—The theoretical speculations in this paper have already appeared (Abstr., 1895, i, 513).

*Dichlorodiamyloxyquinone diamylhemiacetal*, $C_6Cl_2(OH)_2(OC_5H_{11})_4$ (compare this vol., i, 19), is prepared, in the form of its *sodium* salt, by stirring together finely powdered dichlorodiphenoxyquinone (4 grams) and a solution of sodium (1 gram) in amylic alcohol (25 c.c.); the salt remains dissolved, and is precipitated by the addition of ethylic alcohol. The hemiacetal is obtained by treating the sodium salt with acetic acid; it is a white solid, insoluble in water, and rapidly decomposes, yielding a yellow oil. When the sodium salt is warmed with strong hydrochloric acid, *dichlorodiamyloxyquinone*, $C_6Cl_2(OC_5H_{11})_2O_2$, is deposited as a yellow oil, which crystallises with difficulty from acetic acid in irregular, yellowish-red plates; it melts at 53°, and is soluble in most organic solvents. Reduction with zinc dust and glacial acetic acid converts this quinone into *dichlorodiamyloxyquinol*, $C_6Cl_2(OC_5H_{11})_2(OH)_2$, which crystallises in long, thin, white plates, melts at 128°, and dissolves freely in ether, benzene, chloroform, acetone, glacial acetic acid, and carbon bisulphide, slightly in light petroleum, and not at all in water.

It was found that dichlorodibenzyloxyquinone dibenzylhemiacetal is white, although, on account of its great instability, no attempt was made to analyse it.

*Dichlorodibenzyloxyquinone*, $C_6Cl_2(OC_7H_7)_2O_2$, is prepared by mixing a solution of sodium (0·5 gram) in benzylic alcohol (4 c.c.) with absolute ether (150 c.c.), and adding chlorodiphenoxyquinone (2 grams), washing the separated mass with ether, adding it to water, and crystallising the oil, which floats to the surface, from a mixture of benzene and alcohol. It forms long, slender, red plates, melts at 142°, and dissolves freely in alcohol, acetone, benzene, glacial acetic acid, and ethylic acetate, but not at all in ether, light petroleum, or water. By reduction, the quinone yields *dichlorodibenzyloxyquinol*, $C_6Cl_2(OC_7H_7)_2(OH)_2$, which crystallises in white needles, melts at 122—123°, and is freely soluble in alcohol, ether, benzene, glacial acetic acid, and carbon bisulphide, but only slightly in light petroleum and not at all in water.

Full details of the preparation of the blue disodium salt from quinone and sodium phenoxide, and from phenoquinone and sodium $\beta$-naphthoxide (Abstr., 1895, i, 513), are given; the salt is very unstable, ignites spontaneously in the water oven, and is decomposed by water.

*Quinonedinaphthylhemiacetal*, $C_6H_4O_2,(C_{10}H_7OH)_2$, is prepared by mixing benzene solutions of quinone (1·5 grams) and $\beta$-naphthol (3 grams) and evaporating; it crystallises in thin, brown, rectangular plates, melts at 82°, and dissolves freely in ether, chloroform, benzene, glacial acetic acid, and ethylic acetate, but only sparingly in light petroleum; the *sodium* salt is described.

*Thymoquinonequinolhemiacetal*, $C_{10}H_{12}O_2,C_6H_4(OH)_2$, from hydroquinone and thymoquinone in ethereal solution, crystallises in dark brown, rectangular prisms with a green reflection; it melts at 136—137°, and dissolves easily in various solvents, nearly all of which, however, decompose it, dissolving one or other of its constituents.

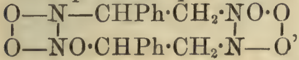
The reaction between thymoquinol and quinone produces quinhydrone. The authors point out that quinhydrone has no sharp melting point, but begins to decompose at 163°, the change being complete at 170°, when a sublimate of quinone, and, above that, one of quinol, is noticed in the melting tube.

A list of substances analogous to phenoquinone, which have been prepared from quinones, is given, together with references to the literature of the subject. A. G. B.

**$\alpha$- and $\beta$-Cinnamene Nitrosite.** By E. A. Sommer (*Ber.*, 1896, **29**, 356—360; compare Abstr., 1895, i, 456).—The molecular weight of the $\beta$-nitrosite agrees with the formula $C_8H_8N_2O_3$, that of the $\alpha$-compound could not be determined on account of its insolubility and instability; when heated, it decomposes into phenylnitroethylene, benzonitrile, nitric oxide, carbonic anhydride, and water; it is, therefore, probably more complex than the $\beta$-derivative, which melts without decomposition. The latter is not changed by distillation with steam; when heated alone, it yields benzonitrile, nitric oxide, carbonic anhydride, water, and, in traces, ammonia. When heated with water under pressure during five hours, both compounds yield benzoic acid, benzonitrile, carbonic anhydride, water, ammonia, and nitrogen; probably the primary products are benzonitrile, carbonic anhydride, and hydroxylamine, and these interact with the result stated. By the action of nitrous acid on cinnamene, two compounds,

$$\mathrm{NO{\cdot}CHPh{\cdot}CH_2{\cdot}NO_2}$$

and $\mathrm{NO_2{\cdot}CHPh{\cdot}CH_2{\cdot}NO}$, might be formed, and by the combination of 2 mols. of these, three substances are theoretically possible; from its decomposition products, the α-nitrosite probably has the formula

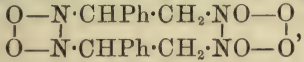


$$\begin{array}{l}\mathrm{O{-}N{-}CHPh{\cdot}CH_2{\cdot}NO{\cdot}O}\\ \;|\quad\;|\qquad\qquad\qquad\quad\;|\quad\;|\\ \mathrm{O{-}NO{\cdot}CHPh{\cdot}CH_2{\cdot}N{-}O}\end{array}$$

, the β-compound being

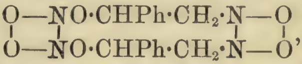
$$\mathrm{NO_2{\cdot}CHPh{\cdot}CH{:}NOH.}$$

Both the other double molecular compounds appear to be formed, the one,



$$\begin{array}{l}\mathrm{O{-}N{\cdot}CHPh{\cdot}CH_2{\cdot}NO{-}O}\\ \;|\quad\;|\qquad\qquad\qquad\quad\;|\qquad|\\ \mathrm{O{-}N{\cdot}CHPh{\cdot}CH_2{\cdot}NO{-}O}\end{array}$$

, readily yields phenylnitroethylene nitric oxide and hydrogen, the second,



$$\begin{array}{l}\mathrm{O{-}NO{\cdot}CHPh{\cdot}CH_2{\cdot}N{-}O}\\ \;|\quad\;|\qquad\qquad\qquad\qquad\;|\quad\;|\\ \mathrm{O{-}NO{\cdot}CHPh{\cdot}CH_2{\cdot}N{-}O}\end{array}$$

, is probably unstable, and should easily change into the β-nitrosite, the decomposition products of which were isolated. The β-nitrosite forms a *silver* salt, and crystallises from boiling concentrated hydrochloric acid in colourless, lustrous needles. Angeli states that when boiled with mineral acids, it is converted into a ketone or aldehyde. The α-nitrosite combines with aniline, forming a crystalline base, $C_{14}H_{14}N_2O_2$; the *hydrochloride*, $C_{14}H_{14}N_2O_2,HCl$, is deposited in white crystals with a pale, rose-coloured reflex; it decomposes when exposed to the air. J. B. T.

**Action of Nitrous acid on Safrole.** By ANGELO ANGELI and ENRICO RIMINI (*Gazzetta*, 1895, **25**, ii, 188—213).—A good yield of safrole α-nitrosite may be obtained by slowly adding dilute sulphuric acid to potassium nitrite solution covered with a solution of safrole in light petroleum, and recrystallising the precipitate; on boiling with alcohol, it yields the β-nitrosite, which is readily converted into hydroxylamine and *nitropiperonylacetone*,

$$\mathrm{CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}NO_2,}$$

by boiling with dilute sulphuric acid. This ketone crystallises in colourless scales melting at 86°, and, when heated with hydroxylamine hydrochloride and sodium carbonate solution, yields *homopiperonyloxamic acid*, $\mathrm{CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}OH}$; this crystallises in minute, white needles, melting and decomposing at 166°, is very soluble in alcohol, and is converted into homopiperonylic acid and hydroxylamine on boiling with dilute sulphuric acid. On heating nitropiperonylacetone with hydroxylamine hydrochloride in presence of but little alkali, safrole β-nitrosite is regenerated.

That nitropiperonylacetone, which readily reduces Fehling's and ammoniacal silver nitrate solutions, is not an aldehyde, but has the constitution assigned above, is evident from the fact that it yields homopiperonylic acid on oxidation with potassium permanganate. On treating it with potassium nitrite and distilling the product in a current of steam, piperonylonitrile, melting at 94°, is obtained, and, on treating nitropiperonylacetone with bromine in acetic acid solution, *bromopiperonylnitroacetone*, $CH_2O_2{:}C_6H_2Br{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}NO_2$, is formed; it melts at 115°, is soluble in acetone or ethylic acetate, and on oxidation with alkaline permanganate yields *bromohomopiperonylic acid*, $CH_2O_2{:}C_6H_2Br{\cdot}CH_2{\cdot}COOH$; this crystallises in lustrous needles melting at 190—191°.

*Bromopiperonylonitrile*, $CH_2O_2{:}C_6H_2Br{\cdot}CN$, is obtained by distilling the product obtained by heating bromopiperonylnitroacetone with sodium nitrite solution in a current of steam; it crystallises in minute, white needles melting at 106°, is very soluble in benzene, acetone, or ethylic acetate, and gives a deep yellow coloration with sulphuric acid.

*Nitropiperonylnitroacetone*, $CH_2O_2{:}C_6H_2(NO_2){\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}NO_2$, prepared by direct nitration, is crystalline, and melts at 170°; it gives a beautiful, blue coloration with potash, and, when the product is distilled in a current of steam, a yellow *nitropiperonylmethane*,

$$CH_2O_2{:}C_6H_2Me{\cdot}NO_2,$$

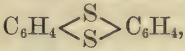
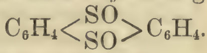
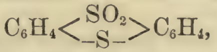
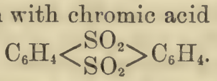
melting at 83°, is obtained.

*Piperonylamidoacetone*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}NH_2$, may be prepared by reducing nitropiperonylacetone with tin and hydrochloric acid; the *hydrochloride*, $C_{10}H_{11}NO_3,HCl$, crystallises in flattened needles, melting and decomposing at 198°, and reduces Fehling's solution, whilst the yellow *picrate*, $C_{10}H_{11}NO_3,C_6H_2(NO_2)_3{\cdot}OH$, melts and decomposes at 160°. The free base is not obtained by adding ammonia to its hydrochloride, but a condensation product, *paradihomopiperonylpyrazine*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}C\lessdot\genfrac{}{}{0pt}{}{CH{:}N}{N{\cdot}CH}\gtrdot C{\cdot}CH_2{\cdot}C_6H_3{:}CH_2O_2$, is formed; it crystallises in small needles, melts at 155—156°, and gives a violet coloration with sulphuric acid.

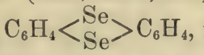
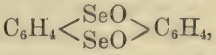
*Diazopiperonylacetone*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CO{\cdot}CH<\begin{matrix}N\\\|\\N\end{matrix}$, is obtained as a yellow oil, together with its decomposition product, homopiperonylic acid, by treating piperonylamidoacetone hydrochloride with sodium nitrite solution; it is decomposed by mineral acids with evolution of nitrogen.

W. J. P.

**Synthesis of Aromatic Selenium Compounds by means of Aluminium Chloride.** By FRIEDRICH KRAFFT and A. KASCHAU (*Ber.*, 1896, **29**, 428—435).—A refutation of Chabrié's criticism (Abstr., 1895, i, 413). The authors have obtained pure phenylic selenide by acting on selenium tetrachloride with benzene in the presence of aluminium chloride at a low temperature and fractionating the product. Diphenylic diselenide is, however, formed at the same time, and the method previously described (Abstr., 1894, i, 89) of preparing the selenide is far more convenient. Chabrié never obtained the selenide pure; it was mixed with diselenide, and this he mistook for hydroselenide. Further, what he described as selenoxide was, in reality, impure selenide. C. F. B.

**Thianthrene (Diphenylene Bisulphide), $C_{12}H_8S_2$, and Selenanthrene. I.** By FRIEDRICH KRAFFT and ROBERT E. LYONS (*Ber.*, 1896, **29**, 435—443).—Thianthrene,  $C_6H_4<\genfrac{}{}{0pt}{}{S}{S}>C_6H_4$, has been obtained by many observers and by various reactions; it is best prepared by slowly adding a benzene solution of sulphur dichloride to a cooled solution of aluminium chloride in benzene; it melts at 158—159°, and boils at 210° under 15 mm. pressure. *Ditolylene bisulphide* was prepared in a similar manner from toluene; it melts at 117—118°, and boils at 228—231° under 14 mm. pressure. Thianthrene is oxidised by boiling with nitric acid of sp. gr. 1·2 to *thianthrene dioxide*,  $C_6H_4<\genfrac{}{}{0pt}{}{SO}{SO}>C_6H_4$. This melts at 229°, is converted by reducing agents into thianthrene, and sublimes at 272—274° under 13 mm. pressure, undergoing at the same time a molecular transformation into *thianthrenemonosulphone* (*diphenylene sulphide sulphone*),  $C_6H_4<\genfrac{}{}{0pt}{}{SO_2}{-S-}>C_6H_4$, which melts at 279°, and is converted by oxidation with chromic acid in boiling acetic acid solution into the disulphone,  $C_6H_4<\genfrac{}{}{0pt}{}{SO_2}{SO_2}>C_6H_4$. This last substance yields thianthrene and sulphurous anhydride when it is heated with sulphur.

Phenylic sulphide can also be oxidised readily to the sulphoxide by boiling it with nitric acid of sp. gr. 1·1. The sulphoxide boils at 199—200° under 10 mm., at 210° under 15 mm., and at about 340° under ordinary pressure, a slight decomposition taking place in the last case. When it is gently boiled for some time in an atmosphere of carbonic anhydride, the sulphide is regenerated; in this respect it analogous to the selenoxide (this vol., i, 304). C. F. B.

**Thianthrene and Selenanthrene, $C_{12}H_8Se_2$. II.** By FRIEDRICH KRAFFT and A. KASCHAU (*Ber.*, 1896, **29**, 443—445).—*Selenanthrene* (*diphenylene diselenide*),  $C_6H_4<\genfrac{}{}{0pt}{}{Se}{Se}>C_6H_4$, is formed by gently heating diphenylenedisulphone (preceding abstract) with selenium in an atmosphere of carbonic anhydride; a steady evolution of sulphurous anhydride accompanies the reaction. It melts at 180—181°, and boils at 223° under 11 mm. pressure. When it is heated at 60—70° with nitric acid of sp. gr. 1·4, the solution, on cooling, yields crystals, which liberate iodine from potassium iodide and have a composition corresponding with the formula $C_{12}H_8Se_2,2HNO_3$; when these crystals are treated with aqueous soda in the cold, and the mixture is saturated with carbonic anhydride and then evaporated under diminished pressure, alcohol extracts *selenanthrene dioxide*,  $C_6H_4<\genfrac{}{}{0pt}{}{SeO}{SeO}>C_6H_4$, from the residue. This melts at 270°, but at the same time loses oxygen and regenerates selenanthrene. C. F. B.

**Nitramines.** By ANTOINE P. N. FRANCHIMONT and H. VAN ERP (*Rec. Trav. Chim.*, 1895, **14**, 235—251; compare Abstr., 1895, i, 587).—*Methyloctylnitramine*, $C_8H_{17}\cdot NMe\cdot NO_2$, obtained by heating octylic iodide (31 grams), methylnitramine (10 grams), potassium hydroxide (10 grams), and absolute methylic alcohol (30 grams) for three days on a water bath, and purified by fractional distillation under diminished pressure, forms a slightly yellow liquid, and distils at 164·5° under 17·5 mm. pressure. When heated with aqueous potash at 160°, it is not appreciably acted on.

*Methylbenzylnitramine*, $CH_2Ph\cdot NMe\cdot NO_2$, after distillation in a vacuum and pressing between filter paper, forms a crystalline mass, which melts at 22·2° and has a slightly aromatic smell. When heated at 150—160° with aqueous potash, it is decomposed into benzaldehyde, methylamine, nitrous acid, and a small quantity of benzoic acid.

*Methylorthonitrobenzylnitramine* crystallises in yellowish needles and melts at 87°. It is only sparingly soluble in ether and light petroleum, but readily in alcohol, chloroform, and benzene. When heated with aqueous potash for seven hours at 150°, it yields methylamine and benzoic acid.

*Methylparanitrobenzylnitramine* melts at 70—71°, and is decomposed when heated with potash at 140—150°, yielding the same compounds as the ortho-compound.

When dimethylnitramine itself is heated with aqueous potash, it yields methylamine, formaldehyde, methylic alcohol, formic acid, and nitrous acid.

The authors think that the decomposition by alkali is first preceded by intramolecular change, $(CH_3)_2N\cdot NO_2 \rightarrow CH_3\cdot NH\cdot CH_2\cdot NO_2$. This, under the influence of the alkali, yields $CH_3\cdot NH_2$ and $OH\cdot CH_2\cdot NO_2$, the latter being further decomposed into formaldehyde and nitrous acid (compare Bamberger, *Ber.*, **26**, 490). J. J. S.

**Action of Sodium on Aromatic Nitriles.** By C. A. ALFRED LOTTERMOSER (*J. pr. Chem.*, 1896 [2], **53**, 143—144).—The author has continued the study of the reactions between aromatic nitriles, aromatic amines and sodium, in benzene, first noticed by Walther (Abstr., 1894, i, 503), and has prepared the following amidines: Orthotolylbenzenylamidine, paratolylbenzenylamidine, phenacetophenylamidine, orthotoluphenylamidine, paratoluphenylamidine, α-naphthophenylamidine, β-naphthophenylamidine. By the action of sodium on benzonitrile in benzene, a compound, which is probably dihydrotetraphenyltriazine, has been prepared. This investigation is proceeding. A. G. B.

**Quantitative Reduction of the Nitro-group to the Hydroxylamine-group.** By HANS WISLICENUS (*Ber.*, 1896, **29**, 494—496).—Nitrobenzene is quantitatively reduced to phenylhydroxylamine when it is dissolved in ether, and treated with amalgamated aluminium filings, water being gradually added, and the mixture cooled by ice. A vigorous action occurs, which should be so regulated that the ethereal solution boils freely. Nitroacetophenone also undergoes reduction under the same conditions (compare Wislicenus and Kaufmann, Abstr., 1895, i, 437, 634). A. H.

**Chemistry of the Diazo-compounds.** By EUGEN BAMBERGER (*Ber.*, 1896, **29**, 446—473).—The author still maintains, in opposition to Hantzsch, that the metallic, normal, and iso-diazo-derivatives are structually, and not merely geometrically, isomeric, and he denotes them respectively by the formulæ Alph·N(:N)·OM and Alph·N:N·OM [Alph = an aromatic radicle, such as $C_6H_5$, $C_6H_4Me$, &c.; M = a metal]; for the salts of diazobenzene with acids he adopts Hantzsch's name of alphyldiazonium salts. In proof of the difference of structure alluded to, further experimental evidence is brought forward. The alkaline normal diazo-salts react with aliphatic alcohols in the cold, yielding diazo-ethers, Alph·$N_2$·OMe, &c.; the iso-salts do not behave in this way. Again, the normal salts are scarcely attacked by sodium amalgam, whereas the iso-salts are readily reduced to hydrazines. But an even more striking difference is seen in the behaviour of these salts with regard to acids. These liberate from the iso-salts the isodiazo-hydroxides, which form either oils or crystals, are colourless, or pale yellow when nitro-groups are present, and are readily dissolved by alkalis with re-formation of the iso-salt; *paranitroisodiazobenzene hydroxide*, $NO_2\cdot C_6H_4\cdot N_2\cdot OH$, has actually been analysed, but the experimental data are to be given in a future paper. From the normal salts, on the other hand, acids at a low temperature liberate diazo-anhydrides; these are bright yellow, extremely unstable substances; when placed on a porous plate, they explode spontaneously as soon as they become even approximately dry; diazobenzene anhydride even exploded once while still in the solution at a temperature of $-18°$, and some moist diazotoluene anhydride at a temperature of 0° was exploded by the concussion due to the explosion, at a distance of 5 ft., of a small sample of the dry substance. They also readily become transformed into diazoamido-compounds. With alkalis, they re-form the colourless normal diazo-salts, whilst with acids, they give the colourless diazonium salts. (In this connection it is interesting to remember that the colourless ethobromide of papaverine, $C_{20}H_{21}NO_4,EtBr$, yields an oxide, $(C_{20}H_{21}NO_4Et)_2O$, which is bright yellow; and also that the oxides of several metals—lead, for example—are coloured, whilst the salts of the same metals are colourless).

*Parachlorodiazobenzene anhydride*, $(C_6H_4Cl\cdot N_2)_2O$, was the most stable of the compounds prepared; it was even possible to analyse it, and with it the reactions of the diazo-anhydrides were studied in greater detail. The other anhydrides prepared were those of paradiazotoluene, diazobenzene, metachlorodiazobenzene, para- and meta-bromodiazobenzene and para- and meta-nitrodiazobenzene; their reactions, so far as they could be studied, resembled those of the anhydride of parachlorodiazobenzene. This yields diazo-ethers with aliphatic alcohols; with benzene, chlorodiphenyl, $C_6H_4ClPh$; with aniline, yellow *chlorodiazoamidobenzene*, $C_6H_4Cl\cdot N_2\cdot NHPh$, melting at 86°, not prepared before (with ammonia, paradiazotoluene anhydride yields bistoluene diazoimide, $(C_6H_4Me\cdot N_2)_2NH$); with bromine, the diazoperbromide; with phenylic hydrosulphide, apparently phenylthiodiazobenzene, $C_6H_4Cl\cdot N_2\cdot SPh$; with iodine, paraiodochlorobenzene, together with some chlorobenzene.

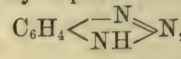
The general method of preparing a diazoanhydride is first to obtain the normal potassium diazo-salt by slowly adding a diazotised solution of the base to a cooled, very strong solution of potassium hydroxide in water, or mixture of the hydroxide with water; the salt is then drained with the aid of a filter pump and preserved in a dry atmosphere free from carbonic anhydride. A concentrated aqueous solution or the salt suspended in water is then treated, at 0° or in a freezing mixture, with 50 per cent. acetic acid, when the diazo-anhydride separates out in yellow, crystalline flakes.

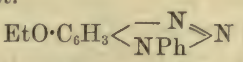
The normal potassium diazo-salts are very readily converted into the iso-salts; at 120—130°, the conversion is complete in 20—30 minutes, and the carbonic anhydride of the air effects the conversion at the ordinary temperature. The presence of alkali does not favour, but even retards, this transformation; when iso-salts are obtained from normal salts by heating them with alkali, which is the usual method of preparation, it is the rise of temperature that brings about the transformation; the alkali only acts by preventing other decompositions taking place as a result of the rise in temperature.

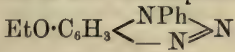
C. F. B.

**Constitution of Azimides [Azoimides].** By THEODOR ZINCKE and BRUNO HELMERT (*J. pr. Chem.*, 1896, [2], **53**, 91—99).—Griess based his conclusion that the azoimides are correctly represented as derivatives of the compound $C_6H_4{<}\begin{matrix}N\\|\\N\end{matrix}{>}NH$ on the fact that he obtained the same azimidobenzoic acid whichever of the two nitrouramidobenzoic acids, [$NO_2$ : NH·NHCONH$_2$ : COOH = 1 : 2 : 4] or

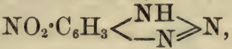
$$[NO_2 : NH{\cdot}CONH_2 : COOH = 1 : 2 : 5],$$

he heated with potash solution; furthermore, the same azimidouramidobenzoic acid was formed when the nitro-acids were reduced and diazotised (Abstr., 1883, 56). It may well be, however, that the similarity between these azimido-acids is so great that even Griess may have been unable to differentiate them. In view of this possibility, the authors decided to repeat Griess' work, and will publish their results, but for the present they content themselves with saying that the characterisation of the azimido-acids in question is so difficult that their identity is hard to establish. It has been possible to obtain two azoimides of the general form $X{\cdot}C_6H_3N_3R$, which are undoubtedly isomerides, and this fact is only explicable on the supposition that Kekulé's typical formula,  $C_6H_4{<}\begin{matrix}-N\\NH\end{matrix}{>}N$, for the azoimides is correct.

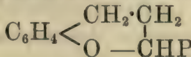
The azoimide,  $EtO{\cdot}C_6H_3{<}\begin{matrix}-N\\NPh\end{matrix}{>}N$ [EtO : NPh = 1 : 4] is prepared by passing through a number of intermediate products, from metadinitrodiphenylamine (compare Nietzki, this vol., i, 164; the authors find that the azoimide $NO_2{\cdot}C_6H_3N_3Ph$, melts at 167°, not at 107° as stated by Nietzki); it crystallises from all solvents in curved needles, and melts at 99°; a saturated alcoholic solution yields no crystals when in contact with the 1 : 3-compound described below, and when it does yield crystals these melt at 99°. The methiodide melts and decomposes at 211°.

The azoimide  $EtO\cdot C_6H_3<\begin{matrix}NPh\\ N\end{matrix}>N$ [OEt : NPh = 1 : 3], is prepared from hydroxyazobenzene, through a number of intermediaries, and has been already described by Jacobsen and Fischer (Abstr., 1892, 840); it crystallises from all solvents except glacial acetic acid, in laminæ, and melts at 107—108°; a saturated alcoholic solution of it yields no crystals when in contact with the 1 : 4-derivative already described, but laminæ, melting at 107—108° afterwards separate. The methiodide melts and decomposes at 177°.

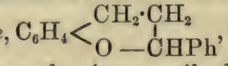
A mixture of these isomerides, crystallises from alcohol, and melts at 70—75°.

The methylnitrazimidobenzene, $NO_2\cdot C_6H_3{:}N_3\cdot CH_3$, prepared from nitrazimidobenzene,  $NO_2\cdot C_6H_3<\begin{matrix}NH\\ N\end{matrix}>N$, was found to melt at 161° and to be identical with that obtained by heating chlorodinitrobenzene, [Cl : $(NO_2)_2$ = 4 : 1 : 3], with methylamine, reducing the dinitromethylaniline, which is formed, and diazotising the nitramidomethylaniline obtained by the reduction. Since the methylnitrazimidobenzene prepared in this way must contain the $NCH_3$ in the para-position relatively to the nitro-group, it follows that the nitrazimidobenzene must contain the NH-group in the para-position relatively to the nitro-group. No isomeride of the nitrazimidobenzene or of the methyl derivative was obtained, and the authors deem it possible that compounds of the type $X\cdot C_6H_3N_3H$ can exist in one form alone.

A. G. B.

**Reduction of Unsaturated Aromatic Ketones and their Conversion into Coumarane Derivatives.** By CARL D. HARRIES and GEORGE J. BUSSE (*Ber.*, 1896, **29**, 375—380; compare Abstr., 1895, i, 279).—*Propyl orthohydroxystyryl ketone* (propylorthocumaroketone), $HO\cdot C_6H_4\cdot CH{:}CH\cdot COPr^a$, is prepared by the condensation of salicylaldehyde and methyl propyl ketone in presence of soda; it crystallises from dilute alcohol, is somewhat soluble in warm water, and melts at 116°. At the boiling point, 1 c.c. of alcohol dissolves 1 gram of the ketone. The yield is 80 per cent. of the aldehyde employed. The *phenylhydrazone*, $HO\cdot C_6H_4\cdot CH{:}CH\cdot CPr^a{:}N_2HPh$, crystallises in small, yellow prisms, melts at 119°, and resembles the ketone in solubility. *Propyl orthohydroxyphenylethyl ketone* (propyldihydrorthocumaroketone), $HO\cdot C_6H_4\cdot CH_2\cdot CH_2COPr^a$, is obtained by the action of sodium amalgam on the unsaturated ketone; it is colourless, crystalline, and melts at 74—75°. The *phenylhydrazone* crystallises in rhombic plates, melts at 149—150°, and is soluble in 7·8 parts of boiling alcohol. The yield is 80 per cent. of the theoretical. The ketone is converted by treatment with zinc and hydrochloric acid into *propyldihydrocoumarane*,  $C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ \quad\ |\\ O\ -CHPr^a\end{matrix}$, a colourless, highly refractive liquid, with a pleasing odour; it boils at 254—257° (760 mm.); the sp. gr. = 0·9946; it is insoluble in alkali, and gives a red coloration with sulphuric acid. The yield is 60 per cent. of the ketone employed.

Phenyl orthohydroxystyryl ketone (orthophenylcoumaroketone), $HO\cdot C_6H_4\cdot CH{:}CH\cdot COPh$, prepared from salicylaldehyde and acetophenone, is the sole product if soda (10 per cent.) is employed as the condensing agent (compare von Kostanecki and Bablich, this vol., i, 239); the yield is 70 per cent. of the aldehyde employed. The *phenylhydrazone* melts at 136°, and its solutions exhibit a blue fluorescence. The *tetrabromo*-derivative is readily prepared by the action of bromine in well-cooled glacial acetic acid solution; it crystallises in yellow needles, melts at 167—168°, and decomposes when boiled with alcohol. von Kostanecki and Bablich state (*loc. cit.*) that the ketone is decomposed by bromine. The *benzoyl*-derivative is crystalline, and melts at 102°.

*Phenylorthohydroxybenzylcarbinol* (phenyldihydrocoumaryl alcohol), $HO\cdot C_6H_4\cdot CH_2\cdot CHPh\cdot OH$, is formed when the above ketone is reduced by means of sodium amalgam; it crystallises in microscopic needles, melts at 96—97°, and gives a red coloration with concentrated sulphuric acid. The yield is 65 per cent. of the ketone. By the action of methylic alcoholic hydrochloric acid on the preceding compound, *dihydrophenylcoumarane*,  $C_6H_4{<}\begin{matrix}CH_2\cdot CH_2\\ O\text{—}CHPh\end{matrix}$, is formed; it is crystalline, melts at 44—45°, has a pleasing smell, does not dissolve in alkali, gives no coloration with sulphuric acid, and, at 18°, 1 gram dissolves in 7 c.c. of alcohol. The yield is 80 per cent. of the alcohol employed.

J. B. T.

**Phenylchloriodopropionic acid and its Derivatives.** By Emil Erlenmeyer (*Annalen*, 1896, **289**, 259—284).—*Phenylchloriodopropionic acid*, $CHPhCl\cdot CHI\cdot COOH$, is formed when cinnamic acid is treated with an ethereal solution of iodine chloride containing hydrogen chloride; it crystallises in colourless leaflets, becomes red at 100°, and melts at 122—123°, yielding gas. Protracted treatment with cold water converts it into phenyliodolactic acid, which is produced immediately by boiling water; aqueous potassium iodide gives rise to cinnamic acid. The *methylic* salt separates from petroleum in colourless crystals, and melts at 97—98°, becoming red; the *ethylic* salt becomes red, and melts at 69—70°.

*β-Ethoxyphenyl-α-iodopropionic acid*, $OEt\cdot CHPh\cdot CHI\cdot COOH$, is obtained by the action of alcoholic potash on the foregoing acid; it crystallises from water in long needles containing $1H_2O$, and becomes red and melts at 138—139°.

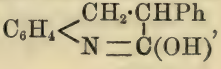
*β-Methoxyphenyl-α-iodopropionic acid* crystallises from water in anhydrous needles, and melts, becoming red at 164—165°.

*Phenyliodohydracrylic acid*, $OH\cdot CHPh\cdot CHI\cdot COOH$, is formed when sodium cinnamate is treated with an aqueous solution of iodine chloride containing hydrogen chloride; it crystallises from benzene in long, colourless prisms, and melts at 140—142° when it becomes red, and evolves gas. The substance decomposes in aqueous solution when the latter is boiled for a protracted period, yielding iodine, phenylacetaldehyde, cinnamene, and cinnamic acid; reduction of phenyliodohydracrylic acid with sodium amalgam gives rise to phenylhydracrylic acid. Boiling aqueous soda converts phenyliodohydracrylic acid into phenylglycidic acid, whilst hot hydrochloric acid gives rise to the *compound*, $C_{18}H_{16}ClIO_4$, which contains phenylchloriodopropionic acid and cinnamic acid in molecular proportion; it becomes red at 70°, and melts at 110—115°, when it decomposes. This substance yields cinnamic, hydrochloric, and phenyliodhydracrylic acids when treated with hot water, and phenylpropionic acid is formed on reduction with sodium amalgam, whilst potassium iodide gives rise to cinnamic acid. M. O. F.

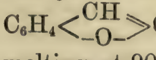
**New Synthesis of Phenanthrene and its Derivatives.** By Robert Pschorr (*Ber.*, 1896, **29**, 496—501).—*α-Phenylorthonitrocinnamic acid*, $NO_2\cdot C_6H_4\cdot CH\dot{:}CPh\cdot COOH$, is obtained by heating orthonitrobenzaldehyde with sodium phenylacetate, acetic anhydride, and zinc chloride. It crystallises in colourless needles, and melts at 193—195°. *α-Phenylorthamidocinnamic acid* crystallises in narrow, yellow prisms, and melts at 185—186°. It dissolves in both acids and alkalis; the *hydrochloride* melts and decomposes at 218°, and the *platinochloride* melts at 220°. The acid also exists in a colourless modification, which is formed when it is recrystallised from water and passes into the yellow form at about 150°. Both forms of the acid are converted into β-phenanthrenecarboxylic acid, melting at 250—252°, when they are diazotised in sulphuric acid solution, and then treated with precipitated copper. The acid produced is identical with that previously described by Japp (Trans., 1880, 84), and yields phenanthrene when distilled.

*α-Phenylorthamido-β-phenylpropionic acid*,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot CHPh\cdot COOH,$$

is formed by the action of sodium amalgam on amidophenylcinnamic acid. It cannot be obtained in the free state, as when the alkaline solution is acidified, *β-phenyldihydrocarbostyril*,  $C_6H_4<\begin{matrix}CH_2\cdot CHPh\\ N=C(OH)\end{matrix}$, which melts at 169°, is formed.

When the alkaline solution is treated with sodium nitrite and sulphuric acid, and then with precipitated copper, a syrupy acid is produced, which yields phenanthraquinone when treated with chromic anhydride and acetic acid. A. H.

*α*-**Benzoylcoumarone.** By E. Rap (*Gazzetta*, 1895, **25**, ii, 285—289).—On adding bromacetophenone to a hot, alcoholic potash solution of salicylaldehyde and concentrating the solution, an *α-benzoylcoumarone*,  $C_6H_4<\begin{matrix}CH\\ O\end{matrix}>C\cdot COPh$, is obtained. This crystallises in long needles melting at 90—91°, and is very soluble in most organic solvents. It yields a *hydrazone*, $C_{15}H_{10}O\dot{:}N_2HPh$, which crystallises in minute yellow needles, melting at 128—129°, and an *oxime*, $C_{15}H_{10}O\dot{:}NOH$, melting at 125—128°; a *substance* melting at 126—135°, is also formed by the action of hydroxylamine.

W. J. P.

**Action of Some Halogen Compounds containing Oxygen on Sodium Benzoicsulphinide (Saccharin).** By HUGO ECKENROTH and KARL KLEIN (*Ber.*, 1896, **29**, 329—332).—The sodium derivative of benzoicsulphinide, $C_6H_4<\substack{CO\\SO_2}>NNa$, reacts with various halogen compounds (compare Fahlberg and List, Abstr., 1887, 835; *Ber.*, **20**, 1596). With monochloracetone, $CH_2Cl\cdot CMeO$, at 100°, it yields *acetonylorthobenzoicsulphinide*, $C_6H_4<\substack{CO\\SO_2}>N\cdot CH_2\cdot CMeO$, which melts at 143°, yields a yellow *phenylhydrazone*, melting at 166°, and a *monobromo*-derivative, melting at 168°, and is hydrolysed to orthosulphobenzoic acid, ammonia, and acetonalcohol. With bromacetophenone, $CH_2Br\cdot COPh$, it reacts at 150°, in a similar way; the product, *phenacylorthobenzoicsulphinide*, melts at 194·5°, yields a yellow *phenylhydrazone*, melting at 168°, and is hydrolysed by alcoholic potash to *phenacylsulphamidobenzoic acid*,

$$COOH\cdot C_6H_4\cdot SO_2\cdot NH\cdot CH_2\cdot COPh,$$

which melts at 160°. C. F. B.

**Diphenylselenone, $SeO_2Ph_2$.** By FRIEDRICH KRAFFT and ROBERT E. LYONS (*Ber.*, 1896, **29**, 424—428).—Diphenylselenoxide (Abstr., 1894, 89), $OSePh_2$, is oxidised when it is boiled with aqueous permanganate, to *diphenylselenone*, which melts at 155°, and boils, with slight decomposition, at 270—271° under 9·5 mm. pressure. This substance loses oxygen when strongly heated, and phenylic selenide is formed. When it is heated with sulphur to 190°, a sudden reaction occurs, phenylic diselenide being formed, and sulphurous anhydride evolved. When it is boiled with strong hydrochloric acid, diphenylselenochloride, $Cl_2SePh_2$, is formed, and chlorine is given off. It also liberates iodine from a solution of potassium iodide. The reactions of diphenylselenone are, in many points, analogous to those of iodoxybenzene, as are those of diphenylselenoxide to those of iodosobenzene.

Nitric acid oxidises phenylic diselenide to *phenylselenious acid*, the *nitrate* of which, $Ph\cdot SeO_2H,HNO_3$ [? $SePh(OH)_2\cdot NO_3$], is a well crystallised substance; the hydrochloride of the corresponding ethylic compound was prepared long ago by Rathke (*Annalen*, **152**, 219). The substance in question has thus basic properties; it also has acid properties, and forms a well defined silver salt. C. F. B.

**Carbazole Derivatives.** By M. LAMBERTI-ZANARDI (*Gazzetta*, 1895, **25**, ii, 359—364).—*Benzoylchlorobromocarbazole*, $C_{12}H_6ClBrNBz$, is prepared by the action of chlorine on Mazzara and Leonardi's benzoylbromocarbazole (Abstr., 1893, i, 349) in acetic acid solution. It crystallises in colourless needles melting at 202°, and is hydrolysed by boiling potash, giving *chlorobromocarbazole*, $C_{12}H_6ClBrNH$, which crystallises in iridescent scales melting at 197—198°; when heated with acetic anhydride in a closed tube at 240°, it yields *acetylchlorobromocarbazole*, $C_{12}H_6ClBrNAc$, which crystallises in lustrous, colourless needles melting at 178—179°.

*α-Benzoyldichlorodibromocarbazole*, $C_{19}H_9NOCl_2Br_2$, obtained by direct chlorination of benzoyldibromocarbazole in presence of iodine, crystallises in opaque, white needles melting at 267—268°; it is accompanied by a *β-isomeride*, which crystallises in small, opaque, white prisms melting at 238—240°, and by another *substance* melting at 190—215°, which could not be purified. W. J. P.

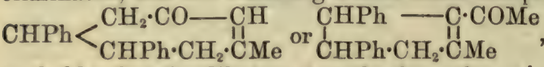
**γ-Carbodiphenylimide.** By J. F. CARL SCHALL (*J. pr. Chem.*, 1896, [2], **53**, 139—142).—The author reviews the criticisms which Miller and Plöchl (Abstr., 1895, i, 415) have passed on his work on the carbodiphenylimides, and claims that the γ-derivative, whether freshly prepared or after long standing, contains at least one physical modification of β-carbodiphenylimide. A. G. B.

**The Diphenylhydroxyethylamine Bases.** By EMIL ERLENMEYER, jun. (*Ber.*, 1896, **29**, 295—298).—The reduction of benzoïnoxime yields a phenylhydroxyethylamine which melts at 161°, along with a second substance melting at 129—130° (Söderbaum, this vol., i, 98), which can be resolved by crystallisation into two isomeric substances, one of which crystallises in thin prisms or three-sided, pointed needles belonging to the hexagonal system, whilst the other crystallises in rectangular tablets. The same two compounds, melting at 129—130°, are also formed, but in different proportions, by the condensation of benzaldehyde with glycocine (Abstr., 1895, i, 596). Three isomerides of phenylhydroxyethylamine have, therefore, been described, and the relations in which they stand to one another have not yet been ascertained. The isomeride melting at 161° is converted, by means of the diazo-reaction, into isohydrobenzoïn, and not into hydrobenzoïn. A base, melting at 128°, has also been observed by Polonowska among the products of the reduction of benzilmonoxime (Abstr., 1888, 485). A. H.

**Reduction of Unsaturated Ketones.** By CARL D. HARRIES and G. ESCHENBACH (*Ber.*, 1896, **29**, 380—388).—Engler and Leist, who discovered benzylideneacetone, state that it is converted into a secondary alcohol when reduced by means of sodium amalgam in dilute alcoholic solution, but the authors only obtained resinous products under these conditions; if the liquid is well cooled and maintained acid by the addition of dilute acetic acid, benzylacetone and *diphenyl*-4 : 5-*octanedione*-2 : 7,

$$COMe{\cdot}CH_2{\cdot}CHPh{\cdot}CHPh{\cdot}CH_2{\cdot}COMe,$$

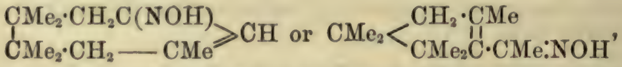
is formed; it crystallises in long, colourless, transparent, triclinic parallelopipeds, melts at 161°, boils at 335—340° under the ordinary pressure, and at 221—222° (10 mm.). It is not volatile with steam, does not combine with sodium hydrogen sulphite, and dissolves in concentrated sulphuric acid with a green coloration. The yield is about 10 per cent. of the diketone and 30 per cent. of benzylacetone; but if aluminium amalgam is employed, the yield of diketone is improved, and benzylacetone is only formed in very small quantity. Attempts to obtain a pyrroline or pyridine derivative were unsuccessful, as, when reduced with sodium and boiling alcohol, or with sodium amalgam in alkaline solution, amorphous compounds are formed; in acid solution, the diketone is not changed; with zinc dust and alcoholic hydrochloric acid, a compound is obtained which melts at 120°, and has not been investigated. The diketone is not oxidised by sodium hypochlorite, potassium dichromate and sulphuric acid, or acetic acid; with chromic anhydride and glacial acetic acid, benzoic acid is formed. With concentrated nitric acid, two yellow, nitrogenous products are obtained, the one by gently heating, the other when the acid is boiled; they melt at about 130° and 67—68° respectively. The *diphenylhydrazone* is sparingly soluble, darkens at 170°, melts at 194°, and could not be recrystallised. The *dioxime* softens at 200°, and melts at 235—237°. No monoxime or monophenylhydrazone could be obtained. By the action of sodium ethoxide on the above diketone, water is eliminated, and the resulting closed chain compound has the formula



$$CHPh\left\langle\begin{array}{l}CH_2\cdot CO\text{---}CH\\ \qquad\qquad\quad\;\, \|\\ CHPh\cdot CH_2\cdot CMe\end{array}\right. \text{or} \begin{array}{l}CHPh\;\text{---}C\cdot COMe\\ |\qquad\qquad\;\; \|\\ CHPh\cdot CH_2\cdot CMe\end{array}$$

, assuming, as appears probable, that the diketone has the formula assigned to it; it crystallises in transparent plates, melts at 87°, boils at 214—215° (8·5 mm.), and at about 330—335° under the ordinary pressure. It is not volatile with steam, and resembles the diketone in its action towards oxidising agents. The yield is 70—80 per cent. of the theoretical. Attempts to reduce the compound by means of sodium in alcoholic solution have not yielded any definite results, and no crystalline oxime or phenylhydrazone has hitherto been obtained.

Mesityl oxide resembles benzylideneacetone in its action towards reducing agents; the product obtained by the action of aluminium amalgam was fractionated, and the portion boiling at 210—220° converted into the *oxime*,



$$\left.\begin{array}{l}CMe_2\cdot CH_2C(NOH)\\ |\\ CMe_2\cdot CH_2\text{---}CMe\end{array}\right\rangle CH \text{ or } CMe_2\left\langle\begin{array}{l}CH_2\cdot CMe\\ \qquad\quad\;\|\\ CMe_2C\cdot CMe{:}NOH\end{array}\right.,$$

which crystallises with $1H_2O$ in long, broad prisms, melts at 156—157°, has a camphor-like odour, readily volatilises at the ordinary temperature, and, in small quantity, may be distilled without decomposition; it does not reduce Fehling's solution, and, when heated with concentrated hydrochloric acid, the ketone is regenerated. The reduction product of mesityl oxide differs from that of benzylideneacetone in stability, the hypothetical compound,

$$COMe\cdot CH_2\cdot CMe_2\cdot CMe_2\cdot CH_2\cdot COMe$$

which is first formed condensing spontaneously to the above closed chain derivative.

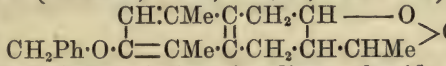
J. B. T.

**Synthesis of Pararosaniline and its Mono-, Di-, Tri-, and Tetra-alkylic Derivatives.** By MAURICE PRUD'HOMME (*Compt. rend.*, 1895, **121**, 891—893).—When the paranitrodiamidotriphenylmethanes are dissolved in hydrochloric acid and treated with zinc dust at the ordinary temperature, they yield complex hydroxylamines [$\cdot CH\cdot C_6H_4\cdot NR_2 : NH\cdot OH = 1 : 4$], and when the latter are heated with hydrochloric acid they yield coloured products, the hydroxylamine group being changed into the amido-group, just as phenylhydroxylamine is converted into paramidophenol, and this notwithstanding the fact that it is the central carbon which occupies the para-position with respect to the hydroxylamine. The products have, therefore, the constitution $[\cdot C(OH)\cdot C_6H_4\cdot NR_2 : NH_2 = 1:4]$. The intermediate leuco-bases are precipitated by adding sodium acetate, and, after the zinc has been removed from the liquid, the colouring matters can be separated by means of alcohol.

To obtain paranitro-compounds corresponding with pararosaniline and its derivatives, 1 mol. of paranitrobenzaldehyde is condensed directly with 2 mols. of aniline or dialkylanilines. The mono- and tri-alkyl-derivatives are obtained by condensing monalkylparanitramidohydroxydiphenyl with aniline or dialkylanilines. Similarly, the dialkylrosanilines may contain alcohol radicles in one or two nuclei.

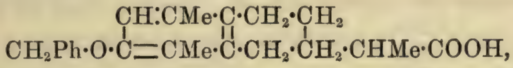
The colour of these derivatives becomes more violet as the number of alkylic radicles in the amido-groups increases, the substitutions having more effect in this respect if they take place in the same nucleus than if they take place in two different benzene nuclei.

C. H. B.

**Desmotroposantonin and the Benzylsantonous acids.** By NICOLA CASTORO (*Gazzetta*, 1895, **25**, ii, 348—359).—*Benzyldesmotroposantonin*,  $\begin{array}{l}\mathrm{CH{:}CMe{\cdot}C{\cdot}CH_2{\cdot}CH \text{——} O}\\ \mathrm{CH_2Ph{\cdot}O{\cdot}C{=}CMe{\cdot}C{\cdot}CH_2{\cdot}CH{\cdot}CHMe}\end{array}\!>\!\mathrm{CO}$, is obtained by allowing an alcoholic solution of sodium ethoxide containing desmotroposantonin and benzylic chloride to remain for some days; it crystallises in white needles melting at 181—182°, and is soluble in ether. Its specific rotation is $[\alpha]_D = +102{\cdot}6°$, and it is readily hydrolysed by boiling with potash, yielding potassium benzyldesmotroposantonate.

The isomeric *benzyldesmotroposantonin*, prepared in a similar manner from isodesmotroposantonin, crystallises in transparent needles melting at 81—82°, has the specific rotation $[\alpha]_D = +136{\cdot}5°$, and is very soluble in ether. It is hydrolysed by boiling potash, giving a salt of benzylisodesmotroposantonic acid.

*Benzyldesmotroposantonous acid*,



$$\begin{array}{l}\qquad\quad\mathrm{CH{:}CMe{\cdot}C{\cdot}CH_2{\cdot}CH_2}\\ \mathrm{CH_2Ph{\cdot}O{\cdot}C{=}CMe{\cdot}C{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}COOH,}\end{array}$$

is prepared by reducing benzyldesmotroposantonin with zinc dust and acetic acid; it crystallises in transparent needles melting at 121—123°, and has the specific rotation $[\alpha]_D = -39{\cdot}3°$. The *sodium* salt crystallises in lustrous laminæ. W. J. P.

**The Anhydride and Decomposition Products of Ethylic Santonite.** By NICCOLÒ RIZZO (*Gazzetta*, 1895, **25**, ii, 290—298).—On distilling ethylic dextrosantonite at 360—370°, hydrogen is evolved, and after treating the distillate with water, the aqueous liquid is found to contain ethylic alcohol and propionic acid; in the oily part of the distillate, ethylic propionate, dimethyldihydronaphthol, and the *anhydride*, $C_{54}H_{42}O_5$, of ethylic dehydrosantonite were found.

W. J. P.

**Conversion of Bromoprotocatechuic acid into a Dibromorthonaphthaquinonecarboxylic acid.** By THEODOR ZINCKE (*J. pr. Chem.*, 1896, [2], **53**, 100—105).—Oxidation of bromoprotocatechuic acid by dilute nitric acid yields a compound of the formula $C_{11}H_4Br_2O_4$, which is probably 3 : 1′-*dibromo*-1 : 2-*naphthaquinone*-3′-*carboxylic acid*, but it remains uncertain whether 3 : 4′ : 1 : 2 : 2′ be not the correct orientation. Much oxalic acid is formed during the oxidation. Towards an alkali, the new compound behaves in part like a bromo-β-naphthaquinone, and in part like a diketone; the first reaction leads to the formation of a hydroxyparaquinone, the second to that of a dibasic acid, $C_{11}H_6Br_2O_6$. Formulæ showing the probable orientation of these compounds, and of those produced by treating them with bleaching powder, are given in the paper. A. G. B.

**Action of Trichloracetic acid on Terpenes.** By ALBERT REYCHLER (*Ber.*, 1896, **29**, 695—697).—When carvene and trichloracetic acid (2 mols.) are brought together, the *compound*,

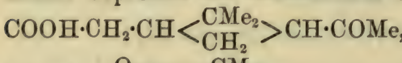
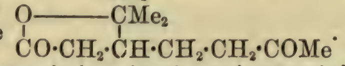
$$(CCl_3\cdot COOH)_2,C_{10}H_{16},$$

is formed; it is optically inactive, crystallises in lustrous leaflets melting at 104°, and yields terpin hydrate when hydrolysed.

Pinene gives rise to borneol when the hydrocarbon is in excess, but in presence of excess of trichloracetic acid, the foregoing compound is produced.

Camphene is converted into a salt of isoborneol. M. O. F.

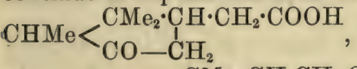
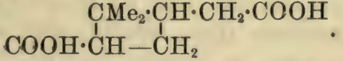
**Orientation in the Terpene Series.** By ADOLF VON BAEYER (*Ber.*, 1896, **29**, 326—329; compare this vol., i, 245).—α-Pinonic acid (*loc. cit.*) is readily obtained by the oxidation of pinene at 30°, it being unnecessary to fractionate the product. If an acid solution is employed at the ordinary temperatures, small quantities of the hydrocarbon may be converted into the crystalline acid in five minutes.

When α-pinonic acid is heated for 30 minutes on the water bath with 10 parts of 50 per cent. sulphuric acid, it is converted into the isomeric lactone (m. p. 63—65°), identical with the substance obtained by Wallach on oxidising terpineol, and by Tiemann and Semmler from the oxidation products of pinene (Abstr., 1895, i, 548). The author expresses the constitution of α-pinonic acid by the formula  $\mathrm{COOH\cdot CH_2\cdot CH}<\substack{\mathrm{CMe_2}\\ \mathrm{CH_2}}>\mathrm{CH\cdot COMe}$, the isomeric lactone having the structure  $\begin{array}{l}\mathrm{O}\text{———}\mathrm{CMe_2}\\ |\qquad\qquad |\\ \mathrm{CO\cdot CH_2\cdot CH\cdot CH_2\cdot CH_2\cdot COMe}\end{array}$. Oxidation of α-pinonic acid with dilute nitric acid gives rise to pinic, oxalic, and terebic acids.

*Hydroxypinic acid*, $C_9H_{14}O_5$, is obtained by treating pinic acid with phosphorus pentachloride and bromine, converting the bromo-acid thus formed into the acetyl derivative by the action of silver acetate, and hydrolysing the acetyl derivative. It crystallises from water in prisms, and melts at 193—194°. M. O. F.

**Pinonic acid.** By FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1896, **29**, 529—544; compare Abstr., 1895, i, 477, and von Baeyer, this vol., i, 246).—The result of oxidising pinene with potassium permanganate is entirely controlled by conditions of temperature, liquid pinonic acid being formed at 6°, whilst von Baeyer's α-pinonic acid is the sole product when the temperature is maintained at 25—40°; the solid acid, however, slowly induces crystallisation in the liquid modification, which thus yields one-half its weight of α-pinonic acid. One decimetre of freshly distilled liquid pinonic acid has $\alpha = +6°$, this rotation being increased to $\alpha = +13°$ when the solid acid has been removed; the latter has $\alpha = +2°$ in a tube of the same length, whilst *l*-pinonic acid, obtained by distilling α-dihydroxydihydrocampholenic acid, has $\alpha = -21°$. The *semicarbazone* of *l*-pinonic acid melts at 231°, and the *oxime* at 125°, or at 131° after successive recrystallisations from water; the *semicarbazone* of *d*-pinonic acid melts at 207°, and the *semicarbazone* of α-pinonic acid melts between 197° and 211°. The formation of methoethylheptanonolide (m. p. 63—65°), which von Baeyer obtained from α-pinonic acid (*loc. cit.*), is observed when all the modifications of pinonic acid are treated with acids, and also occurs when they are distilled slowly under atmospheric pressure.

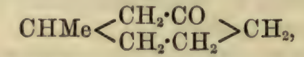
The formation of optically active pinonic acids from active pinenes would seem to indicate that the oxidation process is a simple one, and the authors have shown that the change in question is not dependent on the intermediate formation of α-dihydroxydihydrocampholenic acid; it is probable that *d*- and α-pinonic acids are different configurations of the same substance, and this view is supported by the production of isoketocamphoric and isocamphoronic acids when both acids are oxidised.

The authors have stated that *d*-pinonic acid is indifferent towards alkali hypobromite (Abstr., 1895, i, 478); action does occur slowly, however, and the *l*-acid is also decomposed. The production of bromoform does not necessarily imply the presence of the group $\cdot CO\cdot CH_3$, because the behaviour of iretol (Abstr., 1894, i, 49) and tanacetone (Abstr., 1893, i, 107) has shown otherwise; the authors, therefore, continue to express the constitution of pinonic acid by the formula  $CHMe<\begin{array}{l}CMe_2{\cdot}CH{\cdot}CH_2{\cdot}COOH\\ CO—CH_2\end{array}$, representing pinic acid by the expression  $\begin{array}{l}\qquad\quad CMe_2{\cdot}CH{\cdot}CH_2{\cdot}COOH\\ COOH{\cdot}CH—CH_2\end{array}$. They attribute the formation of pinic acid, on oxidation of pinonic acid with nitric acid, to preliminary molecular rearrangement, and ascribe the conversion of pinonic acid into methoethylheptanonolide to the same cause. This change is illustrated by the transformation of tanacetoketocarboxylic acid into methoethylheptanonolide, and the production of an analogous lactonic acid from tanacetogendicarboxylic acid. M. O. F.

**Terpenes and Ethereal Oils. Pulegone.** By Otto Wallach (*Annalen*, 1896, **289**, 337—361; compare Abstr., 1893, i, 115).—When pulegone is heated with its own volume of anhydrous formic acid in a reflux apparatus, or with water at 250°, acetone is produced along with a *methylcyclohexenone*, $C_7H_{12}O$, which boils at 169°, has the sp. gr. = 0·915 at 21°, and the refractive index $n_D = 1{\cdot}4456$ at the same temperature, whence the molecular refraction $M = 32{\cdot}59$;

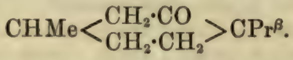
the *semicarbazone* melts at 180°, and the *oxime* at 43—44°. The *cycloheptenamine*, $C_7H_{13}{\cdot}NH_2$, obtained by heating pulegone with ammonium formate (*loc. cit.*), is also produced when the foregoing oxime is reduced in alcoholic solution with sodium; it boils at 151°, and the *carbamide* and *semicarbazone* melt at 178° and 177° respectively. The formation of this primary base is attended with the production of a secondary base, $NH(C_7H_{13})_2$, which boils at 273°, and crystallises in needles (Abstr., 1894, i, 154); the *nitrate* is not very soluble.

Reduction of the foregoing methylhexenone with sodium and alcohol gives rise to *methylcyclohexenol* (*metahydroxyhexahydrotoluene*), $C_7H_{13}{\cdot}OH$, which boils at 77° under a pressure of 17 mm., and at 175—176° under atmospheric pressure; the sp. gr. = 0·914 at 19°, and the refractive index $n_D = 1{\cdot}4581$ at the same temperature, whence the molecular refraction $M = 34{\cdot}04$. The *iodide*, $C_7H_{13}I$, is obtained from the alcohol by means of iodine and amorphous phosphorus; it boils at 100—110° under a pressure of 30 mm., and is converted by quinoline into tetrahydrotoluene, which has been isolated from resin oil by Renard. When the methylcyclohexenone is oxidised with potassium permanganate, it yields an acid, which melts at 69°, and closely resembles the pimelic acid obtained from menthone, which, however, melts at 84—85°. In view of the foregoing observations, the author expresses the constitution of this ketone by the formula



$$CHMe{<}\begin{matrix}CH_2{\cdot}CO\\CH_2{\cdot}CH_2\end{matrix}{>}CH_2,$$

and advocates Semmler's formula for pulegone,



$$CHMe{<}\begin{matrix}CH_2{\cdot}CO\\CH_2{\cdot}CH_2\end{matrix}{>}CPr^{\beta}.$$

The methylcyclohexenone is isomeric with Markownikoff's suberone (Abstr., 1894, i, 160), which yields the *semicarbazone*, melting at 163—164°.

Pulegoneamine (Abstr., 1895, i, 153) boils at 205—210°; the *carbamide* is obtained from the *hydrochloride*, and melts at 104—105°, and the *phenylcarbamide* crystallises from alcohol, and melts at 154—155°.

*Pulegenic acid*, $C_{10}H_{16}O_2$, is obtained by heating a solution of pulegone dibromide in methylic alcohol with sodium for four hours; it undergoes decomposition when boiled at atmospheric pressure, but boils at 155° under a pressure of 13 mm. The sp. gr. = 1·007 at 19°, and the refractive index $n_D = 1{\cdot}48071$ at the same temperature. The *ammonium* salt is white, and the *amide* crystallises in woolly needles, and melts at 121—122°; the *nitrile* boils at 218—220°, has the sp. gr. = 0·8935 at 22°, and the refractive index $n_D = 1{\cdot}47047$ at the same temperature. Reduction of the nitrile converts it into a *base*, having the odour of menthylamine; the *carbamide* melts at 97—99°. The *hydrochloride* of methylic pulegenate boils at 113—116° under a pressure of 12 mm., and solidifies at low temperatures.

The *hydrocarbon*, $C_9H_{16}$, is produced when pulegenic acid is distilled under atmospheric pressure; it boils at 138—140°, has the sp. gr. = 0·79 at 20°, and the refractive index $n_D = 1·44$ at the same temperature, whence the molecular refraction $M = 41·37$. The *nitrosochloride* melts at 74—75°.

The *hydroxylactone*, $C_{10}H_{16}O_3$, obtained by oxidising pulegenic acid with potassium permanganate, melts at 129—130°, and boils at 185° under a pressure of 20 mm.; it is also produced by the action of chromic acid. The *ketone*, $C_9H_{16}O$, is formed when the hydroxylactone is treated with sulphuric acid, carbonic anhydride being eliminated; it boils at 183°, and has the sp. gr. 0·8925 at 21°, and the refractive index $n_D = 1·44506$ at the same temperature. The *carbazone* and *oxime* melt at 169—170° and 94° respectively.

The author compares pulegenic acid with campholenic and fencholenic acids, and develops formulæ for the compounds just described.

M. O. F.

**Oil of Lemon-grass.** By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1895, **121**, 1159—1162).—That portion of the oil of lemon-grass which boils at 107—110° under a pressure of 10 mm. yields a semicarbazone, $C_{11}H_{19}N_3O$, which forms white lamellæ, melting at 171°, and is very slightly soluble in boiling alcohol. That portion of the oil which boils at 110—112° under a pressure of 10 mm. yields three isomeric semicarbazones of the composition

$$C_{10}H_{16}\!:\!N{\cdot}NH{\cdot}CO{\cdot}NH_2.$$

One forms white lamellæ, melting at 171°, and is identical with that obtained from the lower fraction; another crystallises in needles, melts at 160°, and is very soluble in hot alcohol, but only moderately so at the ordinary temperature; and a third forms white needles, which melt at 135°, and are very soluble in cold alcohol.

When the semicarbazone melting at 171°, is boiled with dilute sulphuric acid, it yields paracymene and an aldehyde, which, with semicarbazide, forms the semicarbazone melting at 135°. Under similar conditions, the semicarbazone melting at 135°, yields cymene, and an aldehyde which can be reconverted into the original semicarbazone.

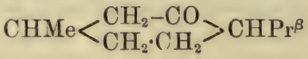
These results are not caused by any stereoisomerism due to nitrogen, and it would seem that oil of lemon-grass contains two acyclic aldehydes, one of which, $CH_2\!:\!CMe{\cdot}CH(COH){\cdot}CH_2{\cdot}CH\!:\!CMe_2$, is converted into the other, $CMe_2\!:\!C(COH){\cdot}CH_2{\cdot}CH\!:\!CMe_2$, by the action of dilute sulphuric acid.

The oil of lemon-grass does not contain an aldehyde of the composition $C_{10}H_{18}O$ (compare Abstr., 1894, i, 400—401).

C. H. B.

**The Camphor Series III: Menthones.** By ERNST BECKMANN (*Annalen*, 1896, **289**, 362—367; compare Abstr., 1889, 722, and 1894, i, 240).—The author has observed that acids and bases exercise an inverting influence on lævo-menthone, transforming it into a dextrorotatory modification (*loc. cit.*); concentrated sulphuric acid, for example, gives rise to a product which is dextrorotatory in the same degree as the original material is lævogyrate. The oxime of the latter, however, has the specific rotatory power $[\alpha]_D = -40·75°$

to −41·97°, whilst the oxime from the dextrorotatory menthone has the specific rotatory power $[\alpha]_D = -4·85°$ to $-6·67°$; it is found, moreover, that as the dextrogyrate character of the menthone becomes intensified, hydroxylamine gives rise to a preponderating amount of the liquid oxime, until finally the product does not yield crystals. The author endeavours to explain the mechanism of this change, basing his considerations on the formula



$$CHMe<{CH_2{-}CO \atop CH_2{\cdot}CH_2}>CHPr^{\beta}$$

for menthone.

Lævo-menthone *semicarbazone* crystallises from alcohol in small needles, melts at 178°, and has the specific rotatory power $[\alpha]_D = -3·67°$ in glacial acetic acid (10 per cent. solution) at 20°; the *semicarbazone* of dextro-menthone has $[\alpha]_D = -3°$ under the same conditions, and melts at 172°, a mixture of the two isomerides melting at 175°. M. O. F.

**Menthones.** By Ernst Beckmann and H. Mehrländer (*Annalen*, 1896, **289**, 367—391).—Oxymenthylic acid,

$$COPr^{\beta}{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}COOH$$

(compare Manasse and Rupe, Abstr., 1894, i, 470), is obtained by oxidising menthone with chromic anhydride, and boils at 292°; it is also produced when menthol is oxidised with potassium permanganate, and was obtained in this way by Arth (Abstr., 1886, 892).

*Menthoximic acid*, $C_{10}H_{18}O_2{:}NOH$, obtained by von Baeyer and Manasse from menthone under the influence of amylic nitrite (Abstr., 1894, i, 522), is produced by the action of hydroxylamine on the foregoing acid; the *sodium* salt is deliquescent, and the *copper* and *silver* salts are amorphous. The *ethylic* salt is a colourless oil, and the *acetyl* derivative is crystalline, and melts at 91°.

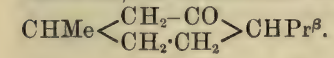
Bromine converts oxymenthylic acid into an oil, which probably has the formula $C_{10}H_{16}O_3Br_2$. The action of bromine on lævo-menthone converts it into a *compound*, $C_{10}H_{17}Br_3O$, a brown oil, which fumes in moist air, and has a disagreeable odour.

The conversion of *l*-menthoneoxime into an isomeride under the influence of phosphorus pentachloride has been observed by Wallach (Abstr., 1894, i, 46 and 337). The same agent acting on *d*-menthoneoxime gives rise to an isomeric *compound*, which crystallises from water, and melts at 88°; a solution in 4 parts of alcohol has the rotatory power $\alpha = -4·9°$ in a 1 decimetre tube at 20°, and the liquid *hydrochloride*, under the same conditions, has the rotatory power $\alpha = -3·67°$. An oily, isomeric *compound* is formed along with the solid substance, and, under the above mentioned conditions, has the rotatory power $\alpha = -1·87°$.

Concentrated sulphuric acid at 100° converts *l*-menthoneoxime into an isomeric *compound*, which melts between 68° and 83°, and although this product appears to consist of a mixture of two substances, attempts to resolve it into constituents have been unsuccessful; it is indifferent towards organic bases, benzoic chloride, phenylcarbamide, sodium amalgam, hydriodic acid, and zinc dust, but yields a hydrochloride, which melts at 91°. Phosphorus pentachloride gives rise to an oil, which, when treated with aqueous soda, yields the compound (m. p. 120°) obtained by the action of phosphorus pentachloride on *l*-menthoneoxime (Abstr., 1894, i, 46). M. O. F.

**The Menthones; Conversion into Thymol.** By ERNST BECKMANN and H. EICKELBERG (*Ber.*, 1896, **29**, 418—421).—*Dibromomenthone*, $C_{10}H_{16}Br_2O$, is obtained by adding bromine (2 mols.) to *l*- or *d*-menthone dissolved in four parts by weight of chloroform, and, after adding ether and agitating with soda, allowing the reddish-brown oil obtained on evaporation to lose hydrogen bromide spontaneously; it separates from alcohol in colourless crystals, and melts at 79—80°. A 3·05 per cent. solution in carbon tetrachloride has the specific rotatory power $[\alpha]_D = +199{\cdot}4°$. Zinc dust is without action on dibromomenthone in alcoholic solution, but in presence of glacial acetic acid, menthone is regenerated; hydroxylamine converts it into the *oximido*-compound, $OH{\cdot}C_{10}H_{16}Br{:}NOH$, which crystallises from light petroleum, and melts at 136—137°.

When dibromomenthone is heated for five minutes with boiling quinoline (6 mols.), thymol is produced, and the authors conclude, therefore, that menthone has the constitution expressed by the formula



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{CHPr^{\beta}}.$$

M. O. F.

**Halogen Derivatives of Camphene and Hydrocamphene.** By ERNST JÜNGER and A. KLAGES (*Ber.*, 1896, **29**, 544—547).—When camphene hydrochloride is treated with glacial acetic acid, isobornylic acetate is formed; the fact that bornylic chloride yields the same product, is probably owing to initial regeneration of camphene (compare Bertram and Walbaum, Abstr., 1894, i, 204).

Camphene hydrochloride, which melts at 165°, unites with bromine forming an oil which yields bromocamphene when distilled with quinoline; this substance, which has been described by Wallach (*Annalen*, **230**, 293), boils at 226—227°, has the sp. gr. = 1·265 at 15°, the refractive index $n_D = 1{\cdot}52605$ at 15°, and the molecular refraction M = 52·36.

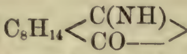
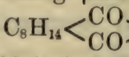
From the similarity exhibited by isobornylic chloride and bornylic chloride, the authors regard isoborneol and its derivatives as geometrically isomeric with the corresponding borneol derivatives.

M. O. F.

**Isobornylic Chloride and Camphene Hydrochloride.** By ALBERT REYCHLER (*Ber.*, 1896, **29**, 697—699).—Both camphene and isoborneol yield isobornylic chloride when hydrogen chloride is led into the alcoholic solution; although indifferent towards alcoholic hydrogen chloride, phosphorus pentachloride converts borneol into bornylic chloride, and the author, therefore, regards isobornylic chloride and camphene hydrochloride as identical, and stereoisomeric with bornylic chloride. M. O. F.

**Derivatives of Camphoric and Hemipinic acids.** By SEBASTIAAN HOOGEWERFF and WILLEM A. VAN DORP (*Rec. Trav. Chim.*, 1895,

**14**, 252—275).—The authors have prepared α-camphoramic acid by a method differing but slightly from that recommended by Auwers and Schnell (Abstr., 1893, i, 525). It is best purified by conversion into its hydrochloride by passing dry hydrogen chloride into an alcoholic solution of the acid; the pure hydrochloride is then decomposed by treatment with water. It crystallises in colourless plates, melts at 176—177°, and is fairly soluble in hot water, readily in acetone and alcohol, sparingly in ether, chloroform, and benzene. Its rotatory power in alcoholic solution is $[\alpha]_D = +45°$. Nitrous acid converts it into camphoric acid. The *silver salt* forms colourless crystals; the *copper* salt crystallises with $4H_2O$ in small spheres.

*α-Camphorisoimide hydrochloride*,  $C_8H_{14}<\genfrac{}{}{0pt}{}{C(NH)}{CO—}>O,HCl$, is obtained when the α-camphoramic acid is heated with about four times its weight of acetic chloride (compare Abstr., 1893, i, 599). It is somewhat unstable, and is rapidly transformed by water into α-camphoramic acid. It forms an *aurochloride*, $C_9H_{15}NO_2,AuCl_4$, which is a yellow, crystalline compound, and melts at 120—130°. When the hydrochloride is decomposed with potassium or ammonium hydroxide, it is converted into a salt of *cyanolauronic acid*, $CN\cdot C_8H_{14}\cdot COOH$. This acid crystallises in orthorhombic prisms, and melts at 151—152° without undergoing decomposition. When rapidly distilled, it passes over unaltered, but if kept at the boiling point for some time it is transformed into camphorimide,  $C_8H_{14}<\genfrac{}{}{0pt}{}{CO}{CO}>NH$, and when boiled with concentrated hydrochloric acid it is hydrolysed to camphoric acid. Its alcoholic solution is optically active, $[\alpha]_D = +67° 30'$. Its *silver* salt is only slightly sensitive to light. The *methylic* salt melts at 40—42°, and the *ethylic* salt at 24—27°. Cyanolauronic acid, when reduced with sodium and alcohol, yields the acid $NH_2\cdot CH_2\cdot C_8H_{14}\cdot COOH$, the *platinochloride* of which forms yellowish plates, and does not melt below 270°.

*β-Camphoramic acid* is obtained, together with a small quantity of the isomeric α-acid, on treating camphorimide with sodium hydroxide (compare Noyes, Abstr., 1894, i, 339). It crystallises in prisms or plates, melts at 180—181° (Noyes 182—183°), is readily soluble in alcohol, acetone, and hot water, sparingly in ether, benzene, and chloroform; its alcoholic solution has a rotatory power $[\alpha]_D = +60°$. When treated with nitrous acid, it yields ordinary dextro-camphoric acid.

*β-Camphorisoimide hydrochloride* is obtained when the above acid is heated with acetic chloride, and yields a yellow, crystalline *aurochloride.* On treating the hydrochloride with aqueous ammonia and then acidifying, *cyanodihydrocampholytic acid*, $CN\cdot C_8H_{14}\cdot COOH$, is formed; this acid crystallises in monoclinic plates, melts at 109—111°, and has a rotatory power $[\alpha]_D = +18° 12'$.

*Methyl-β-camphoramic acid*, $NHMe\cdot CO\cdot C_8H_{14}\cdot COOH$, is obtained on treating camphormethylimide (compare Abstr., 1893, i, 599) with sodium hydroxide. It crystallises with $1H_2O$ in oblong plates, loses its water at 80°, and then melts at 177—178°; it is readily soluble in alcohol and acetone, sparingly in benzene, and still more sparingly in ether.

*β-Camphormethylisoimide*, obtained by the action of phosphorus oxychloride on methyl-β-camphoramic acid, crystallises in colourless needles, melts at 85—86·5°, and boils at 255—258° (uncorr.) with only slight decomposition; it dissolves in dilute hydrochloric acid, but is quickly hydrolysed to the methylamic acid. It yields a *hydrochloride* and also an *aurochloride*.

*α-Hemipinamic acid*, $NH_2 \cdot CO \cdot C_6H_2(OMe)_2 \cdot COOH$ [= 2 : 3 : 4 : 1], is formed, together with a small quantity of the isomeric β-acid, when hemipinic anhydride is dissolved in aqueous ammonia and then acidified with a mineral acid. It crystallises in colourless needles with $2H_2O$, which it loses at 80°, and then melts at 160—162°, at the same time undergoing decomposition and yielding hemipinimide, which melts at 220°. The acid is moderately soluble in alcohol, sparingly in acetone, and very sparingly in benzene and ether. Hot water dissolves it, but at the same time converts it into the imide. The *silver* salt of the α-acid is a colourless, crystalline precipitate.

*Cyanodimethoxybenzoic acid*, $CN \cdot C_6H_2(OMe)_2 \cdot COOH$ [= 2 : 3 : 4 : 1], is obtained from the α-acid in exactly the same way as cyanolauronic acid from α-camphoramic acid. It crystallises in colourless needles, melts at 207—208°, and is readily converted into the α-hemipinamic acid on exposure to moist air.

*β-Hemipinamic acid*, $NH_2 \cdot CO \cdot C_6H_2(OMe)_2 \cdot COOH$ [= 1 : 3 : 4 : 2], is best prepared by treating hemipinimide with sodium hydroxide. It forms hexagonal plates, and, when anhydrous, melts at 142°, probably yielding the imide. A mixture of the α- and β-acids is best separated by dissolving in aqueous ammonia and adding hydrochloric acid when the β-acid separates. The *silver* salt of the β-acid crystallises in colourless needles, is soluble in hot water, and is not rapidly darkened on exposure to light.

*Cyanodimethoxybenzoic acid*, $CN \cdot C_6H_2(OMe)_2 \cdot COOH$ [= 6 : 2 : 3 : 1], prepared in the same way as the isomeric acid, crystallises in slender needles which contain $2H_2O$, and when anhydrous melts at 81—82°.

The authors consider that the formation of α-amic acids on treating the anhydride of unsymmetrical dicarboxylic acids (camphoric and hemipinic) with ammonia, and the formation of the isomeric β-amic acids on treating the corresponding imides with caustic soda are readily accounted for on the supposition that one of the carboxylic groups of the dibasic acid has stronger acid properties than the other.

J. J. S.

**The Root of Rumex nepalensis.** By OSWALD HESSE (*Ber.*, 1896, **29**, 325).—In consequence of an announcement by A. G. Perkin (Trans., 1895, 1084) of his intention to investigate the substances contained in this root, the author states that he has already obtained the following compounds from it, and is engaged in their examination: (1) $C_{15}H_{10}O_4$, yellow plates, melting at 186—188°; (2) $C_{16}H_{12}O_4$, orange needles, melting at 136°; (3) $C_{18}H_{16}O_4$, greenish-yellow prisms, melting at 158°. The first is soluble in sodium carbonate, the other two are insoluble. C. F. B.

**Metallic Salts with Organic Bases.** By FRITZ REIZENSTEIN (*Zeit. anorg. Chem.*, 1896, **11**, 254—263; see also Abstr., 1895, i, 121).—*Tetrapyridine nickelous chloride*, $NiCl_2,4C_5NH_5$, is obtained by boiling hydrated nickelous chloride, previously heated for some time at 145°, with an excess of pyridine; the bluish-green mass thus obtained is washed with absolute alcohol and ether. It crystallises from pyridine in bright blue needles.

*Pyridine nickelous chloride*, $NiCl_2,C_5NH_5$, is obtained by heating the preceding compound at 115—120°.

Tetrapyridine cobaltous chloride, previously prepared from anhydrous cobaltous chloride, can also be obtained by adding pyridine to an aqueous solution of cobaltous chloride; it crystallises from the mixture in deep red crystals. Monopyridine cobaltous chloride is formed on heating the tetrapyridine compound at 115—120°, or the dipyridine compound at 104—106°; it is a bright blue powder.

*Quinoline cobaltous chloride*, $CoCl_2,C_9NH_7$, is obtained by heating the tetraquinoline compound at 115—120° for one hour and then at 120—135° for one hour.

Cobalt and nickel sulphate also give compounds with pyridine, which will be described later. Hydrated compounds of the above type have not been obtained; when the monhydrate or dihydrate of cobaltous chloride is treated with pyridine or quinoline, dipyridine or diquinoline cobaltous chloride is obtained. E. C. R.

**Pyridine Alkyl Iodides.** By ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1896, **18**, 91—96).—These compounds are formed on treating pyridine with the required alkyl haloïd, the methyl compound being prepared by heating the mixture in a flask attached to a reflux condenser. The ethyl compound is best prepared by occasionally shaking the mixture in a flask at the ordinary temperature, whilst the propyl compounds are made by heating the mixture in a sealed tube at 130°.

Pyridine methiodide forms flat needles, sometimes aggregated in rosettes, very soluble in water, alcohol, methylic alcohol, chloroform, acetone, and glacial acetic acid, insoluble in ether, benzene, and carbon bisulphide. It is slightly deliquescent and melts at 117°.

Pyridine ethiodide forms colourless plates melting at 90·5°; it is permanent or slightly deliquescent, soluble in water, alcohol, acetone, and glacial acetic acid, from which it crystallises, and slightly soluble in ethylic acetate, insoluble in ether, benzene, carbon bisulphide, and chloroform.

*Pyridine propiodide* forms colourless plates and melts at 52—53°; it is deliquescent, soluble in water, alcohol, amylic alcohol, ethylic acetate, and benzene, insoluble in ether and chloroform.

*Pyridine isopropiodide* forms colourless crystals, soluble in water, 95 per cent. alcohol, and ethylic acetate, but less freely in absolute alcohol, amylic alcohol, or chloroform, insoluble in ether; it melts at 114—115°. L. DE K.

**Dipyridine Trimethylene Dibromide.** By R. F. FLINTERMANN and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1896, **18**, 28—35).—The authors have prepared this compound, $CH_2(CH_2{\cdot}C_5NH_5Br)_2$, by acting on pyridine (2 mols.), boiling at 116—118°, with trimethylene bromide (1 mol.), with the addition of one-fifth of the volume of absolute alcohol to the mixture. The compound forms completely in about a week in the cold, but is more rapidly obtained by heating in a sealed tube for four hours at 105—110°.

The light brown, crystalline mass is drained, washed with alcohol, and once recrystallised from alcohol, then being nearly white; a pure, white product is, however, obtained when the action takes place in the cold. It is very soluble in water, less soluble in alcohol and ether, and but very slightly so in chloroform. Kept in an open vessel for weeks, it shows no indication of decomposition, only getting slightly moist. The crystals melt and gradually decompose at 225—226°.

The molecular weight was determined by the cryoscopic method, using phenol as solvent. L. DE K.

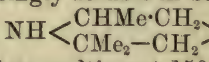
**Synthesis of Tetrahydropyridine Derivatives and their Conversion into Piperidine Derivatives.** By ANDREAS LIPP (*Annalen*, 1895, **289**, 173—253; compare Abstr., 1892, 1243).—Normal acetobutylic alcohol (*hexane*-2 : 6-*ketol*) has been already described by the author (Abstr., 1886, 218); the *anhydride*, $C_6H_{10}O$, which boils at 106—107° under a pressure of 720 mm., is identical with methyldehydrohexone (Perkin, jun., Trans., 1887, 723). The *phenylhydrazone* of acetobutylic alcohol is obtained from the alcohol itself or the anhydride, and forms a yellowish, viscous oil, which becomes brown on exposure to the air; the *oxime* is a colourless syrup, which has no action on Fehling's solution until treated with sulphuric acid. The *acetate* boils at 231—232° under a pressure of 713 mm., and yields a white, crystalline *compound* with sodium hydrogen sulphite; the *benzoate* is a limpid, colourless liquid, which decomposes when heated under atmospheric pressure.

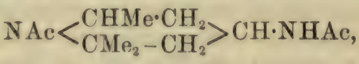
*Methyl benzamidobutyl ketone*, $COMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NHBz$, is obtained by the action of benzoic chloride on $\Delta^2$-tetrahydropicoline (*loc. cit.*) in presence of alkali; it crystallises in needles and melts at 75—76°. When heated at 170—180° with fuming hydrochloric acid, it is resolved into benzoic acid and tetrahydropicoline. The *oxime* crystallises in needles or prisms and melts at 87°.

Methyl phenylamidobutyl ketone *platinochloride* crystallises in needles, and at 200—202° decomposes, evolving gas; the *picrate* melts at 124—125°, and the *oxime* at 68—69°, the *phenylhydrazone* being a yellowish, viscous oil. Reduction of the ketone in acid solution gives rise to 1-phenyltetrahydropicoline, whilst, in presence of an alkali, *phenylamidomethylbutylcarbinol*, which melts at 44—45° and boils at 320—322° (720 mm. pressure), is formed. M. O. F.

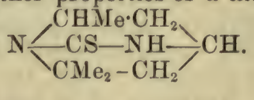
**The Oximes of the Cyclic Acetone Bases: Paramidotrimethylpiperidine.** By CARL D. HARRIES (*Ber.*, 1896, **29**, 521—529).

—*Triacetonaminoxime*, $C_9H_{18}N_2O$, is obtained by the action of hydroxylamine on triacetonamine, and crystallises in large, white, six-sided prisms, melting at 152—153°; it forms crystalline salts with hydrochloric and sulphuric acids. *Benzylidenediacetonaminoxime*, $C_{13}H_{18}N_2O$, crystallises in lustrous, four-sided tablets, melting at 140—141°, and is only sparingly soluble in boiling water.

*Vinyldiacetonaminoxime*,  $NH<\genfrac{}{}{0pt}{}{CHMe\cdot CH_2}{CMe_2-CH_2}>C\colon NOH$, crystallises in translucent, four-sided tablets, melting at 150—151°. When reduced with alcoholic hydrogen chloride, zinc dust, and a little water, it is converted into 4-*amido*-2 : 2 : 6-*trimethylpiperidine*, which forms a crystalline mass, melts at 25—26°, and boils at 60° (pressure = 7·5 mm.). The base has a faint odour of piperidine, and rapidly combines with the carbonic anhydride of the air, forming a carbamate. The *hydriodide* of the base crystallises in fascicular groups of white prisms, and is moderately soluble in water; the *hydrochloride* is readily soluble in water; the *aurochloride* crystallises in red, oblique, six-sided tablets, and is sparingly soluble in water, whilst the *platinochloride* and *picrate* are also crystalline. The base forms both a *normal* and an *acid oxalate*, the latter being very hygroscopic. 4-*Acetamido*-2 : 2 : 6-*trimethylpiperidine* crystallises in cubes, melting at 206—207°; it is strongly basic, and forms an *aurochloride*, melting at 235° with decomposition. The *diacetyl compound*,



$$NAc<\genfrac{}{}{0pt}{}{CHMe\cdot CH_2}{CMe_2-CH_2}>CH\cdot NHAc,$$

is formed when the base is heated with excess of acetic anhydride at 160°; it forms small prisms, melts at 88—89°, boils at 160—170° (pressure = 8 mm.), and has basic properties, forming a crystalline *aurochloride*. This diacetyl compound is accompanied by another basic substance, which boils at about 200° (pressure = 8 mm.), and is probably an anhydro-derivative. The base does not yield a diazo-compound with sodium nitrite and an acid, whilst with amylic nitrite it yields a nitroso-derivative, the imido-group having taken part in the reaction. When heated with chloroform and alcoholic potash, no carbylamine derivative is produced. The base reacts with carbon bisulphide, forming a *thiocarbamate*, $C_9H_{18}N_2S_2$, which crystallises from water in prisms and melts at 187—188°. When this salt is treated with mercuric chloride, it yields the hydrochloride of a new base. The latter crystallises in small prisms and melts at 79—80°. It has not the smell or other properties of a thiocarbimide, and probably has the constitution  $N\begin{matrix}\diagup CHMe\cdot CH_2\diagdown\\ —CS—NH—\\ \diagdown CMe_2-CH_2\diagup\end{matrix}CH.$

A. H.

**Isopipecoline.** By ALBERT LADENBURG (*Ber.*, 1896, **29**, 422—424).—The reasoning is given that led the author to regard as isopipecoline what Marckwald (this vol., i, 253) asserts to be merely a mixture of *d*- and *l*-pipecoline. The author maintains that his own conclusion is correct.

C. F. B.

**Derivatives of Pipecolinic acid.** By RICHARD WILLSTÄTTER (*Ber.*, 1896, **29**, 389—392).—Ethylic pipecolinate, $COOEt\cdot C_5NH_{10}$, is prepared from *nitrosopipecolinic acid*, which is oily; it is a colourless, highly refractive, viscid liquid, with an odour resembling that of acetamide; it boils at 216—217° (corr.), and at 107° under a pressure of 20 mm., has a strongly alkaline reaction, is volatile at the ordinary temperature, and miscible with alcohol, water, and ether. In presence of dilute sulphuric acid, the ethylic salt slowly decomposes potassium permanganate, and is extremely readily hydrolysed. H. Meyer's description of it is incorrect. The yield is 90 per cent. of the theoretical. The acid melts at 264°, and has a neutral reaction; Ladenburg states that it has an acid reaction, and melts at 259°. Unless diluted, methylic iodide and ethylic pipecolinate react with explosive violence, ethylic pipecolinate hydriodide, ethylic methylpipecolinate, and *ethylic* n-*methylpipecolinate methiodide* being formed; the latter crystallises in colourless prisms, melts at 127—128°, and, when distilled, is resolved into its constituents. It is readily soluble in soda, and is hydrolysed, but not otherwise decomposed, when the solution is boiled; when fused with potash, it yields dimethylamine, but the reaction proceeds with difficulty; its stability under these conditions is in marked contrast to the corresponding derivatives of tropinic acid, ecgonine, and anhydroecgonine, which also contain a reduced pyridine ring (compare this vol., i, 265). The *aurochloride* of the *methochloride*,

$$COOEt\cdot C_5NH_9Me,MeAuCl_4,$$

crystallises in thin, flat, yellow plates melting at 78°. The corresponding salt of the *acid* crystallises in golden, lustrous, tetragonal plates and prisms, melting and decomposing at 227—228°.

J. B. T.

**3-Nitroquinoline and 3-Amidoquinoline.** By ADOLPH CLAUS and LUDWIG SCHNELL (*J. pr. Chem.*, 1896, [2], **53**, 106—126).—Contrary to expectation, 3-nitroquinoline could not be directly nitrated to a dinitroquinoline. When dry hydrogen bromide is passed into the chloroform solution of 3-nitroquinoline, the *hydrobromide*, $NO_2\cdot C_9NH_6,HBr$, separates in the form of a heavy, white, crystalline powder melting at 245°, and at the same time losing hydrogen bromide. By shaking this salt with bromine in chloroform, the *dibromide*, $NO_2\cdot C_9NH_6,HBr,Br_2$, is obtained; it forms yellowish-red crystals, and is converted into 3′ : 3-*bromonitroquinoline* when heated at 170—180° until the hydrogen bromide is almost entirely expelled. The bromonitroquinoline crystallises from hot water in yellowish needles, melts at 165°, and sublimes; the *methiodide* crystallises from hot water in brilliant, red needles, and melts at 235°. The bromo-derivative shows the same resistance to nitration that is exhibited by the parent nitroquinoline; justification for the adopted orientation is given. 3 : 3′-*Bromamidoquinoline* is best prepared by mixing the nitro-compound with water and the calculated quantity of iron powder, so as to form a thick paste, which is then thoroughly mixed with a few drops of glacial acetic acid; after the action is over, a porous mass is left, from which the amido-compound is extracted by chloroform or ether. It crystallises in colourless needles, melts at

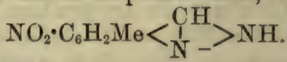
106°, is not volatile with steam, and dissolves freely in hot water or alcohol; its salts are yellow. By brominating the amido-derivative in chloroform, 4 : 3′ : 3-*dibromamidoquinoline* is obtained in the form of a *hydrobromide* (m. p. 210°), from the solution of which it may be precipitated by alkalis; it crystallises in slender, lustrous needles, which are greenish in mass, and melts at 146°; evidence of the orientation is given.

3-Amidoquinoline melts at 114°, not 140° (Bielstein, *Org. Chem.*, **3**, 752); the *methiodide* is obtained as a yellow, crystalline precipitate, and melts at 199°. By acetylising 3-amidoquinoline, 3-*acetamidoquinoline* is formed; it crystallises in silky, colourless, slender needles, melts at 75°, sublimes unchanged, and dissolves freely in water and alcohol, but only sparingly in benzene, light petroleum, &c. 3-*Benzamidoquinoline* crystallises in brilliant, colourless laminæ, melts at 130°, and dissolves easily in hot alcohol; it sublimes unchanged, but is not volatile with steam. 2 : 3-*Bromamidoquinoline*, prepared by brominating the amidoquinoline in glacial acetic acid, crystallises in colourless laminæ, melts at 67°, does not sublime unchanged, and is not volatile with steam; it dissolves easily in alcohol, but only sparingly in hot water; evidence of its orientation is given. 2 : 3-*Bromacetamidoquinoline* is obtained by brominating acetamidoquinoline; the *hydrobromide* separates first in yellow crystals, which melt at 241°; the base crystallises from hot water in brilliant, bronze coloured laminæ, and melts at 165°. *Dibromo*-3-*amidoquinoline* melts at 170°, and *dibromo*-3-*acetamidoquinoline* at 159°; the orientation of the second bromine atom in these two compounds is not yet ascertained. A. G. B.

**3-Methylindazole.** By SIEGMUND GABRIEL and ROBERT STELZNER (*Ber.*, 1896, **29**, 303—309).—When nitrometaxylidine,

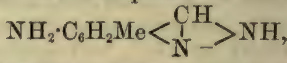
$$(Me_2 : NH_2 : NO_2 = 1 : 3 : 4 : 5),$$

is treated with sodium nitrite in presence of dilute sulphuric acid, it is converted into 1 : 3-*nitromethylindazole*,



$NO_2{\cdot}C_6H_2Me\Big<\begin{matrix}CH\\ |\\ N-\end{matrix}\Big>NH.$

This substance was first obtained by Müller (*Diss. Berlin*, 1883), who, however, ascribed to it the formula $C_3H_8N_3O_2$. When it is reduced with tin and hydrochloric acid, it yields 4 : 1 : 3-*chloramidomethylindazole*, which crystallises in plates with a satiny lustre, and melts at 195°, whilst the *acetyl derivative* melts at 154°. When reduced with ammonium sulphide, on the other hand, the nitro-compound is converted into 1 : 3-*amidomethylindazole*,



$NH_2{\cdot}C_6H_2Me\Big<\begin{matrix}CH\\ |\\ N-\end{matrix}\Big>NH,$

which crystallises in colourless needles, and melts and decomposes at 172°. The base dissolves both in acids and alkalis, and forms a *picrate*, which melts and decomposes at 183°. The *dibenzoyl derivative* forms yellow crystals, and melts at 186—187°. 3-*Methylindazole* crystallises in slender, colourless needles, melts at 116—117°, and boils at 293—294° (pressure = 747 mm.). The *nitrosamine*, $C_8H_7N_3O$, forms yellow needles, which melt at 61°, and give Liebermann's reaction. *Methylindazole picrate* melts at 159—160°.

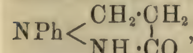
The chlorinated bases formed by the reduction of nitro-compounds by means of hydrochloric acid and tin or stannous chloride, are usually para-derivatives. Ortho-compounds may, however, be formed when the para-position is occupied. It is probable that the formation of these compounds is preceded by the production of a hydroxylamine derivative, and this reacts with the acid, yielding a chloride, which then passes by intramolecular change into a para-chloro-derivative. A. H.

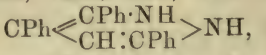
**Rejoinder to R. von Rothenburg: Isomerism in the Pyrazole Series.** By Ludwig Knorr (*J. pr. Chem.*, 1896, [2], **53**, 127—132). —Polemical (compare Abstr., 1895, i, 303, 395, 571). A. G. B.

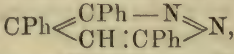
**Constitution of 1 Phenylpyrazolone.** By Carl D. Harries and George Loth (*Ber.*, 1896, **29**, 513—520).—*Ethylic β-anilidopropionate*, $NHPh\cdot CH_2\cdot CH_2\cdot COOEt$, is readily obtained by heating ethylic β-iodopropionate with aniline; it is a light yellow oil, which boils at 175° (pressure = 18 mm.). *Ethylic nitroso-β-anilidopropionate* is an oil, which gives Liebermann's reaction. When the nitroso-compound is dissolved in ether and reduced with aluminium amalgam, it is converted into *ethylic as-β-phenylhydrazidopropionate*,

$$NH_2\cdot NPh\cdot CH_2\cdot CH_2\cdot COOEt,$$

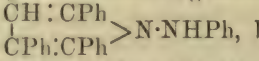
which boils at 174—175° (pressure = 9 mm.), and is readily soluble in dilute alkalis and mineral acids. The *picrate* crystallises in fascicular needles melting at 131—132°. The *oxalate* melts at 107°, and is readily soluble in water. The oxalate reacts with potassium cyanate to form the *semicarbazide of the hydrazido-compound;* this crystallises in cubic crystals melting at 163—164°, and is insoluble in acids and alkalis. The *phenylthiosemicarbazide* melts at 71—74°.

When ethylic phenylhydrazidopropionate is treated with alcoholic sodium ethoxide, it is converted into 1 : 3-phenylpyrazolidone,  $NPh<\begin{matrix}CH_2\cdot CH_2\\ NH\cdot CO\end{matrix}$, melting at 119—121°. The *hydrochloride* of this substance crystallises in nacreous plates melting at 163°. 2 : 1 : 3-*Acetylphenylpyrazolidone* crystallises in colourless prisms melting at 66—67°. When phenylpyrazolidone is treated with sodium nitrite, the solution neutralised with ammonia, and silver nitrate added, a yellow substance is obtained, which, however, is not homogeneous, but a mixture of the silver salts of 1 : 3-phenylpyrazolone and of nitrophenylpyrazolone, produced by the action of traces of nitric acid. The 1 : 3-phenylpyrazolone obtained from the phenylpyrazolidone melts at 153°, and forms a hydrochloride, which crystallises in slender needles melting at 111°. It was found impossible to prepare the 1-phenylpyrazolone-4-azobenzene described by Rothenburg (Abstr., 1894, i, 145). (4- ?) *Nitro*-1 : 3 *phenylpyrazolone* is formed when phenylpyrazolone is dissolved in dilute nitric acid, and crystallises in long, thread-like needles melting at 190—192°. 2 : 1 : 3-*Acetylphenylpyrazolone* crystallises in colourless, fan-shaped needles melting at 62—63°. A. H.

**Action of Hydrazine and Phenylhydrazine on 1 : 4-Diketones.** By Alexander Smith [and in part James H. Ransom] (*Annalen*, 1896, **289**, 310—337).—3 : 4 : 6-*Triphenyldihydropyridazine*,  $\mathrm{CPh}<\substack{\mathrm{CPh\cdot NH}\\ \mathrm{CH:CPh}}>\mathrm{NH}$, is obtained by acting on desylacetophenone with hydrazine for one hour; it crystallises in yellow needles and when heated rapidly melts at 186—188°, decomposing at 190°. Along with this substance there is produced the *monhydrazide* of desylacetophenone, which is also formed when the pyridazine derivative is heated with glacial acetic acid; it crystallises from alcohol in slender needles, and melts at 168°, yielding when distilled, a *compound* which crystallises in white needles, and melts at 181°.

3 : 4 : 6-*Triphenylpyridazine*,  $\mathrm{CPh}<\substack{\mathrm{CPh-N}\\ \mathrm{CH:CPh}}>\mathrm{N}$, crystallises in lustrous, white plates, and melts at 171°; it is easily obtained when the dihydro-derivative is distilled, or oxidised with chromic and acetic acids. The substance is also formed during the preparation of triphenyldihydropyridazine, and may be produced by adding potassium nitrite to a solution of the latter compound in cold glacial acetic acid.

With James H. Ransom.—The *hydrazone* of phenacyldesoxypiperonoin (Abstr., 1893, i, 219), $C_{30}H_{22}N_2O_4$, crystallises in yellow needles, and melts at 166°.

1 : 3 : 4 : 6-Tetraphenyldihydropyridazine, obtained by the action of phenylhydrazine on desylacetophenone (Trans., 1890, 647), has been regarded by Klingemann as having the constitution of an anilidopyrroline derivative,  $\substack{\mathrm{CH:CPh}\\ |\\ \mathrm{CPh:CPh}}>\mathrm{N\cdot NHPh}$, because phenylhydrazine converts $\alpha\beta$-dibenzoylstilbene into anilidotetraphenylpyrroline (Abstr., 1892, 995); the author describes experiments, however, which are in agreement with the pyridazine formula. The *benzoyl* derivative, $C_{35}H_{26}N_2O$, crystallises from glacial acetic acid in white needles, and melts at 139—140°; it is indifferent towards phenylhydrazine, alcoholic potash, and hydrochloric acid. An additive *compound*, $C_{28}H_{23}N_3O_2$, obtained from tetraphenyldihydropyridazine by the action of nitrous acid, crystallises in pale yellow needles which melt and decompose at 262°; boiling alcoholic potash converts it into a *compound* which crystallises in rhombohedra melting at 133°, and is identical with the substance obtained by the action of acetic chloride on triphenyldihydropyridazine. Tetraphenyldihydropyridazine is indifferent towards sodium in ethylic alcohol, but is reduced in presence of boiling amylic alcohol, yielding two *compounds* which melt at 212° and 157° respectively; the absence of aniline among the products has been established. Boiling dilute nitric acid converts tetraphenyldihydropyridazine into the *compound* $C_{28}H_{21}N_3O_3$, which melts and decomposes at 255°.

1 : 3 : 4-*Triphenylpyrazole* is obtained by the dry distillation of 1 : 3 : 4 : 6-tetraphenyldihydropyridazine; it crystallises from glacial acetic acid in small prisms, and melts at 185°. This substance does not arise from the decomposition of an anilidopyrroline derivative, because neither triphenylpyrroline nor aniline is found in the distil-

late; the gas produced during distillation, moreover, is free from ammonia, and contains but little nitrogen. M. O. F.

**Indulines and Safranines.** By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1896, **29**, 361—371; compare this vol., i, 50, and Kehrmann, Abstr., 1895, i, 527).—The indulines and safranines are readily differentiated by their behaviour towards concentrated sulphuric acid, the former giving violet or blue colours, whilst the simple safranines all dissolve with a green coloration. The bye-products obtained in the preparation of indazine and phenylmauveïne (Abstr., 1895, i, 608) are probably true indulines, as they dissolve with a blue colour in sulphuric acid. Objection is taken to Kehrmann's view that salts of indulines and indone (rosinduline) are derived from the orthoquinoïdal azonium form, whilst the induline bases, free from oxygen and the indones, are paraquinoïdal anhydrides of amido- or hydroxyazonium bases. The basicity of many of these compounds must be due to the imido-group and not to the phenazine nitrogen, otherwise it is difficult to understand the feebly basic properties of aposafranone and rosindone which form no acetates, but contain the group NPh; the azonium formula also indicates the presence of a free amido-group in the salts of aposafranine and rosinduline, but the former do not react with nitrous acid, aldehydes, or ketones. No special significance can be attached to the formation of hydrates by the above compounds, as this property is common to many organic bases; rosaniline and rosinduline hydrates closely resemble one another, the former is converted into the anhydrous compound by heating at 40—50°, or when extracted with ether or benzene from its aqueous solution. The formulæ of aposafranine hydrochloride and rosinduline hydroxide are, therefore, $\overset{4}{N}H_2Cl{:}C_6H_3{<}\begin{matrix}\overset{1}{N}\text{—}\\ \underset{2}{N}Ph\end{matrix}{>}C_6H_4$ and $OH{\cdot}\overset{4}{N}H_2{:}C_{10}H_5{<}\begin{matrix}\overset{1}{N}\text{—}\\ \underset{2}{N}Ph\end{matrix}{>}C_6H_4$ respectively.

It has been previously shown (Abstr., 1893, i, 613) that "benzeneinduline," $C_{18}H_{13}N_3$, and "phenylinduline," $C_{24}H_{17}N_3$, are formed by the interaction of aposafranine salts and aniline; these compounds have now been identified as *anilidoaposafranine*,

$$\overset{5}{N}HPh{\cdot}C_6H_2(\overset{4}{N}H){<}\begin{matrix}\overset{1}{N}\text{—}\\ \underset{2}{N}Ph\end{matrix}{>}C_6H_4,$$

and *anilidophenylaposafranine*, $\overset{5}{N}HPh{\cdot}C_6H_2(\overset{4}{N}Ph){<}\begin{matrix}\overset{1}{N}\text{—}\\ \underset{2}{N}Ph\end{matrix}{>}C_6H_4$. The former crystallises from dilute alcohol; by the action of acids, it yields anilidoaposafranone, $\overset{5}{N}HPh{\cdot}C_6H_2\overset{4}{O}{<}\begin{matrix}\overset{1}{N}\text{—}\\ \underset{2}{N}Ph\end{matrix}{>}C_6H_4$, and then hydroxyaposafranone, $\overset{5}{O}H{\cdot}C_6H_2\overset{4}{O}{<}\begin{matrix}\overset{1}{N}\\ \underset{2}{N}\end{matrix}{>}C_6H_4$, which was previously termed "benzeneindonehydrate." The *methoxy*-derivative crystallises in red, stellate needles or well developed prisms, melts at 246—248°, and gives an orange solution with concentrated sulphuric acid. Anilidophenylaposafranine is formed in considerable quantity from aniline and aposafranine under the conditions previously given, but only in traces if alcohol is present. Paratoluidine and aposafranine, in the absence of alcohol, yield paratoluidoaposafranine and *toluidotolylaposafranine* which, from its resemblance to the phenyl derivative, should have a similar constitution; it crystallises in green, lustrous plates, and melts at 238—240°.

Paraphenylenediamine and aposafranine, in presence of alcohol, yield the compound $NH_2\cdot C_6H_4\cdot \overset{5}{N}H\cdot C_6H_2(\overset{4}{N}H)<\begin{matrix}\overset{1}{N}—\\ \underset{2}{N}Ph\end{matrix}>C_6H_4$, which crystallises from benzene in bluish-green prisms, melts and decomposes at 227°, and gives, with concentrated sulphuric acid, a reddish-violet coloration which changes to red on dilution. The *hydrochloride* is crystalline, and, in aqueous solution, has a brownish-red colour. By the action of dilute sulphuric acid at 170°, the base is resolved into paraphenylenediamine and hydroxyaposafranine.

Orthophenylenediamine and aposafranine hydrochloride yield *phenylfluorindine*, $C_6H_4<\begin{matrix}NH\\ —N\end{matrix}>C_6H_2<\begin{matrix}N—\\ NPh\end{matrix}>C_6H_4$, the formation of which is probably preceded by that of a compound isomeric with the preceding; it is very sparingly soluble, and crystallises from ethylic benzoate in needles of a golden bronze lustre; in mineral acids, the solution is blue, with a bluish-red fluorescence. The *hydrochloride* is crystalline, and its alcoholic solution is blue, with a red fluorescence. This synthesis confirms the authors' formulæ previously given to the fluorindines.

The preparation of anilidophenylaposafranine has been already described (see above); it is also formed from aniline and anilidoaposafranine, by the oxidation of azophenine, and by the elimination of the amido-group from "amidophenylinduline." The molecular weight in naphthalene agrees with the above formula; the earlier determinations were made in benzene solution, and the results were too low. The *nitrate* crystallises in green, lustrous prisms. Amidophenylinduline, $\overset{5}{N}HPh\cdot C_6H_2(\overset{4}{N}Ph)<\begin{matrix}\overset{1}{N}—\\ \underset{2}{N}Ph\end{matrix}>C_6H_3\cdot \overset{4}{N}H_2$, has been previously described, but the position of the amido-group was not determined; this has now been accomplished (see below). The *hydrochloride* and *nitrate* crystallise with $\frac{1}{2}$ and $1H_2O$ respectively. By the action of dilute sulphuric acid at 170° on the base, amidohydroxyaposafranine (this vol., i, 50) is formed; the *nitrate* crystallises in thick, greenish, lustrous prisms; the *diazo*-derivative yields hydroxyaposafranone when heated. With dilute sulphuric acid at 230—250°, amidophenylinduline yields *dihydroxyaposafranone*, which crystallises in brownish-yellow needles, melts above 280°, and dissolves in soda with a reddish-yellow coloration. With alkalis, amidophenylinduline yields hydroxyaposafranone, which was identified as "safranol" by means of the methoxy-derivative, which softens at

240° and melts at 266°, not at 240° as previously stated. A second base, probably *anilidosafranol*, is also formed in small quantity; it crystallises in blue, lustrous prisms, and, like anilidoaposafranone, dissolves in concentrated sulphuric acid, yielding a dull green solution which changes successively to green and violet-red when diluted. The *hydrochloride* is green, lustrous, and crystalline. The constitution of amidophenylinduline (anilidomauveïne), as regards the position of the amido-group, is shown by the following facts: It is formed by the fusion of amidoazobenzene, and from azophenine and paraphenylenediamine; phenosafranine, mauveïne, phenylmauveïne, and amidophenylinduline hydrochlorides by the action of aniline, yield the same induline (m. p. 286—288°), which is the final product of the action of aniline on amidoazobenzene, phenylamidoazobenzene, and azobenzene. The *acetate* of this *induline* crystallises in characteristic, flat prisms of a coppery bronze lustre. The *hydrochloride* and *hydrobromide* have also been prepared. The formula of the induline is probably $C_{42}H_{32}N_6$, as, in its formation from amidophenylinduline and phenylmauveïne the primary product is probably $\overset{4}{\mathrm{N}}\mathrm{Ph{:}C_6H_3}<\begin{matrix}\overset{1}{\mathrm{N}}\text{—}\\ \underset{2}{\mathrm{NPh}}\end{matrix}>\mathrm{C_6H_3{\cdot}}\overset{4}{\mathrm{N}}\mathrm{HPh}$, which melts at 245°, has been previously described, and yields a soluble *acetate*.

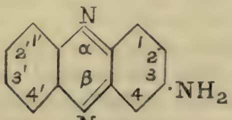
J. B. T.

**Safranines.** By GEORGE F. JAUBERT (*Compt. rend.*, 1895, **121** 947—948; compare Abstr., 1895, i, 219 and 278).—The oxidation of a mixture of paraphenylenediamine and methylmetaphenylenediamine yields the methyl derivative of phenylene-red, but if metatolylenediamine is substituted for the methylmetaphenylenediamine, the dimethylsafranine, $\overset{4}{\mathrm{N}}\mathrm{H{:}C_6H_2}\overset{5}{\mathrm{Me}}<\begin{matrix}\overset{1}{\mathrm{N}}\text{—}\\ \underset{2}{\mathrm{NMe}}\end{matrix}>\mathrm{C_6H_3{\cdot}}\overset{4}{\mathrm{N}}\mathrm{H_2}$, is obtained in considerable quantity. It has all the characteristic properties of the safranines, dyes mordanted cotton a ponceau red, and yields a diazo-derivative with nitrous acid. The diethyl derivative is obtained in a similar way, and the ethylsafranol is prepared by the action of nitrosophenol on ethylmetamidophenol.

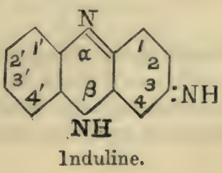
$\alpha$- and $\beta$-naphthasafranols are obtained by the action of nitrosophenol on metahydroxyphenyl-$\alpha$-naphthylamine, or the $\beta$-derivative. If the sulphonic derivative of metahydroxydiphenylamine is used, phenosafranolsulphonic acid is formed.

C. H. B.

**Nomenclature of Phenazine Dyes.** By GEORGE F. JAUBERT (*Ber.*, 1896, **29**, 414—418).—The phenazine derivatives can be divided into two classes: eurhodines, with an orthoquinonoïd structure, and indulines, with a paraquinonoïd structure.



Eurhodine.



Induline.

*Eurhodines.*—The derivative, with an additional $NH_2$ in 3′, is to be called amidoeurhodine ("phenylene-red"). When the $NH_2$ of eurhodine is replaced by OH, the new compound is to be called *eurhodol;* amido- and hydroxy-eurhodol have, in addition, $NH_2$ and OH respectively in 3′.

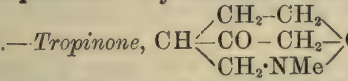
*Indulines.*—The 3′-amido-derivative, amidoinduline, is the simplest possible "safranine." If the NH of induline is replaced by O, the compound is to be called *indulone;* amido- and hydroxy-induline ("safranol") have, in addition, $NH_2$ and OH respectively in 3′. Substitution of the H of the NH-group in the middle ring is to be indicated by the vowel o; thus, phenoindulone ("safranone"). In phenylindulone some other hydrogen atom would be replaced by phenyl.

It is pointed out that in order to get a "safranine" dye from an induline derivative it is necessary that the amido-group should go into the *para*-position relatively to the α-nitrogen atom, just as, in order to get a pararosaniline compound from diamidotriphenylmethane, the third amido-group must go to the para-position relatively to the methane carbon atom. C. F. B.

**Dithiazolic Derivatives.** By CHARLES LAUTH (*Compt. rend.*, 1895, **112**, 1152—1154).—The compound $C_6H_4{<}\substack{S\\N}{\geqslant}C\cdot C{\leqslant}\substack{S\\N}{>}C_6H_4$, obtained by Hofmann by heating acetanilide with sulphur, contains two groups ${<}\substack{S\\N}{\geqslant}C$, and might, therefore, be expected to yield colouring matters similar to the primulines. When treated with a mixture of nitric and sulphuric acids, it yields a mixture of two isomeric dinitroderivatives, one of which melts at about 210° and the other at about 290°, and this, when reduced by stannous chloride in presence of an acid at 60—100°, yields two isomeric diamido-derivatives, which can be separated by the difference in their solubility in water. The less soluble of the two shows brilliant, green fluorescence in alcoholic solution; the other is non-fluorescent. Both the bases and their salts alter when their solutions are boiled, hydrogen sulphide being liberated. Hydrogen sulphide is also evolved when the bases are treated with an acid reducing agent.

Both bases are dyes, and impart a beautiful, yellow colour to animal fibres, and also to unmordanted cotton. Their diazo-derivatives also yield a varied series of colouring matters, which dye unmordanted cotton; β-naphthol-α-sulphonic acid, for example, yields a red dye with the diazo-derivative of the soluble base, and amido-α-naphtholdisulphonic acid yields a blue dye with the diazo-derivative of the less soluble base. The colours on fabrics are somewhat resistant to the action of acids and alkalis, but fade when exposed to light. C. H. B.

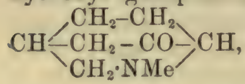
**Constitution of Tropine.** By ALBERT LADENBURG (*Ber.*, 1896, **29**, 421—422).—Willstätter (this vol., i, 265) has misunderstood the author's reasoning; he would not otherwise maintain that tropinic acid contains a pyridine ring with a tertiary nitrogen atom, whilst the author has shown it to form an open chain with a secondary nitrogen atom. C. F. B.

**Tropinone.** By RICHARD WILLSTÄTTER (*Ber.*, 1896, **29**, 393—403).—*Tropinone*,  $CH\left\langle\begin{matrix}CH_2\text{--}CH_2\\ CO-CH_2\\ CH_2\cdot NMe\end{matrix}\right\rangle CH$, is prepared by the cautious oxidation of tropine by means of chromic anhydride in glacial acetic acid solution; it is colourless, soon turns yellow when exposed to air, but is stable towards potassium permanganate; it is readily soluble, and volatile at the ordinary temperature, and distils readily with steam if the solution contains free potash; it has a characteristic basic odour, forms flat crystals, melts at 41—42°, and boils at 224—225° (corr.). Tropine boils at 233° (corr.). The ketone is an active base, and liberates ammonia from its salts; it forms white clouds with hydrogen chloride, and, like granatonine, gives a mirror with silver nitrate; it precipitates the hydroxides from copper, ferric, and aluminium salts, and with lead nitrate gives a flocculent precipitate, which becomes granular and crystalline when warmed, and dissolves readily in hot water. With phosphomolybdic acid, a greenish-yellow, flocculent precipitate is formed; with tannin, a white one; with potassium dichromate and sulphuric acid, a green coloration is obtained. The yield is 80 per cent. of the theoretical.

The *mercurochloride* crystallises in long, silky, lustrous needles; the *potassioiodide* is at first brown and oily, but readily crystallises in prisms. The *hydrochloride* crystallises in lustrous, stellate prisms, melting and decomposing at 188—189°. The *picrate* is deposited in long, lustrous, yellow needles, melting and decomposing at 220°; it is conveniently employed for the purification of tropinone. Tropine picrate is more readily soluble than the preceding compound, is strongly pleochroic, and gradually decomposes when heated. *Tropinone platinochloride* crystallises at the ordinary temperature in orange-red pyramids, and from hot solutions in feathery aggregates of prisms, melting and decomposing at 191—192°. The *aurochloride* is deposited in tabular aggregates of sulphur-yellow, microscopic prisms; it melts and decomposes at 160—170°, and, when boiled with water, deposits gold. The *phenylhydrazone* is oily. The *methiodide* forms highly refractive, crystalline aggregates, resembling those of sodium chloride, and melts and decomposes at 263—265°; when boiled with sodium carbonate, it is readily converted into dimethylamine and dihydrobenzaldehyde; the same products are obtained by treating the methiodide with silver oxide and boiling the resulting *tropinonemethylammonium hydroxide*, which is strongly alkaline. The dihydrobenzaldehyde appears to be identical with Einhorn's $\Delta^{4\cdot6}$-compound from anhydroecgonine dibromide. The *aurochloride* of *tropinone methochloride* crystallises in yellow prisms, melting and decomposing at 205—206°.

*Tropinone oxime* crystallises from light petroleum in slender, stellate prisms, melting at 111—112°. It has both basic and feebly acidic properties, and readily reduces silver salts when warmed with them. The *hydrochloride* crystallises in prisms and melts and decomposes at 242°. The *methiodide* is deposited in long, colourless, highly refractive prisms; it melts at 236°, but a portion decomposes previously, and is more stable than tropinone methiodide, as it is not decomposed when boiled with alkali. The *aurochloride* of the *methochloride* crystallises in slender, pale yellow prisms, melting and decomposing at 182°. The *ammonium hydroxide* reduces silver salts, but is not decomposed by alkali.

The preceding results are in complete accord with Merling's formula for tropine, but not with Ladenburg's, which indicates that it is a primary alcohol (compare this vol., i, 65). The relationship of tropine to tropinone and tropinic acid is similar to that of borneol to camphor and camphoric acid, and tropinone shows a striking analogy with granatonine, $C_9H_{15}NO$ (Tanret's pseudopelletierine), both in general properties and derivatives; granatonine methiodide, for example, yields, by the action of alkali, dihydroacetophenone. The formula given above for tropinone corresponds with that regarded by Merling as the more probable for tropine, but, as the position of the hydroxyl group in this is undetermined, the alternative formula,



$$CH{<}\begin{matrix}CH_2{-}CH_2\\CH_2{-}CO\\CH_2{\cdot}NMe\end{matrix}{>}CH,$$

may prove to be correct.

J. B. T.

**Replacement of the Hydroxyl Group in Cinchona Alkaloïds by Hydrogen.** By WILHELM KOENIGS (*Ber.*, 1896, 372—374; compare this vol., i, 264).—Quinine and cinchonidine, when treated with phosphorus pentachloride, yield the compounds

$$OMe{\cdot}C_9NH_5{\cdot}C_{10}H_{15}ClN \text{ and } C_9NH_6{\cdot}C_{10}H_{15}ClN$$

respectively, from which, by the action of iron filings and dilute sulphuric acid at the ordinary temperature, *deoxyquinine*,

$$OMe{\cdot}C_9NH_5{\cdot}C_{10}H_{16}N,$$

and *deoxycinchonidine*, $C_9NH_6{\cdot}C_{10}H_{16}N$, are formed. No anhydro-bases are produced, as in the case of cinchonine. Deoxyquinine crystallises from ether or dilute alcohol with $2\frac{1}{2}H_2O$, in colourless, slender needles, melts at about 52°, and deliquesces over sulphuric acid; in dilute solution, it fluoresces like quinine. The salts are readily soluble, and crystallise with difficulty; the *platinochloride* darkens without melting, at 260°. The *hydriodide* is crystalline. Deoxycinchonidine crystallises in colourless, rhombic plates, and melts at 61°. The *platinochloride*, *zincochloride*, *cadmiochloride*, and *mercurichloride* crystallise readily in needles. Both bases give the quinine reaction with chlorine water and ammonia. Quinine and cinchonidine are lævorotatory, conquinine and cinchonine dextrorotatory; all four chlorides are dextrorotatory, as are the anhydro-bases quinenine, cinchonidenine, quinidenine, and cinchenine, but the sign of rotation of the deoxy-bases is the same as that of the alkaloïds from which they are derived; these facts accord with Pasteur's view, that the alkaloïds contain two asymmetric carbon atoms in the "second half" of the molecule; to one of these the hydroxyl group is probably linked, and, as the deoxy- and anhydro-bases differ in the sign of their rotation, this carbon atom must be a tertiary one.

J. B. T.

# Organic Chemistry.

**Investigations on American Petroleum. Chemistry of the Berea Grit Petroleum.** By Charles F. Mabery and Orton C. Dunn (*Amer. Chem. J.*, 1896, **18**, 215—235).—Analyses of the Berea Grit sandstone: I, white oil sand; II, blue caprock, yield the following figures.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | $\underbrace{\text{CaO. MgO.}}$ | $H_2O$ (combined) | Total. |
|---|---|---|---|---|---|---|
| I. | 92·30 | 4·80 | 0·92 | 0·28 | 1·40 | 99·70 |
| II. | 91·80 | 4·60 | 1·50 | 0·34 | 1·80 | 100·04 |

Samples of oils obtained from the principal sandstones of the lower coal measures which overlie the Berea Grit sandstone, namely, from the 140, 300, 500, and 700 foot strata, were collected in fractions of 25°, and the percentage of distillate, specific gravity, bromine absorption, and hydrogen bromide eliminated, determined in each case.

Three specimens of the Berea Grit petroleum from the 1,500 foot oil sand were treated in the same manner, and two analyses of gas evolved from this formation were made.

| | $CO_2$. | CO. | O. | N. | Illuminating hydrocarbons. | $CH_4$. | Total. |
|---|---|---|---|---|---|---|---|
| I. | 0·30 | 0·40 | 4·00 | 1·20 | 2·60 | 92·00 | 99·70 |
| II. | 0·10 | 0·80 | 0·30 | 1·00 | 0·70 | 97·00 | 99·90 |

The fractionation of this oil yielded a hydrocarbon, $C_{10}H_{22}$, boiling at 162—163° (760 mm.), and of sp. gr. = 0·7475 at 20°. Another hydrocarbon of this formula was also isolated, boiling at 173—174°, and with a sp. gr. = 0·7517 at 20°.

A hydrocarbon, $C_{11}H_{24}$, was obtained from the fraction 194—196°. This boils at 195° (760 mm.), and has a sp. gr. = 0·7622 at 20°.

From the higher fractions, a hydrocarbon, $C_{12}H_{26}$, boiling at 215° (760 mm.), of sp. gr. = 0·7746, was isolated. J. F. T.

**Artificial Production of Asphalt from Petroleum.** By Charles F. Mabery and J. H. Byerley (*Amer. Chem. J.*, 1896, **18**, 141—150).—In the ordinary process of distilling petroleum, the residue is a porous coke. The authors describe a process, originated by F. X. Byerley, for obtaining more valuable products by slow distillation in a current of air at a temperature not exceeding 650° F. In this way, asphalts of various degrees of viscosity (some of which closely resemble native bitumen) are formed, but no free carbon.

In a note on the determination of sulphur in organic substances by combustion in air (compare Mabery, Abstr., 1895, ii, 136), it is stated that substances containing a high percentage of sulphur yield sulphurous as well as sulphuric acid. In these cases, a little hydrogen peroxide should be added before titration. A. E.

**Action of Hydrogen Bromide on Hydrocarbons of the Series $C_nH_{2n-2}$.** By WLADIMIR IPATIEFF (*J. pr. Chem.*, 1896, [2], **53**, 145—168).—The main product of the action of a glacial acetic acid solution of hydrogen bromide on dimethylisoallylene (b. p. 39·5—41°) cooled to 0° is *β-dimethyltrimethylenic dibromide*, $CMe_2Br{\cdot}CH_2{\cdot}CH_2Br$; it boils at 74—75°, and its sp. gr. = 1·6975 at 0°/0°; its constitution was ascertained by converting it into a glycol, which proved to be identical with that prepared by Kondakoff from a corresponding dichloride (Abstr., 1893, i, 541). A closed chain hydrocarbon is obtainable from this dibromide, and will be treated of hereafter.

The hydrocarbon, $C_6H_{10}$, obtained by heating the bromohexylene, $CMe_2{:}CBr{\cdot}CH_2Me$, which boils at 138—141°, with alcoholic alkali in a sealed tube at 150°, may be trimethylisoallylene, $CMe_2{:}C{:}CHMe$, or methylisopropylacetylene, $CHMe_2{\cdot}C{\vdots}CMe$, since Faworsky has shown that conversion of such a hydrocarbon into a disubstituted acetylene is frequent under this treatment (Abstr., 1888, 798). If the bromine be removed from the bromohexylene by powdered caustic potash, intramolecular change need not, according to Faworsky, be feared; this method was, therefore, adopted, with the result that the *trimethylisoallylene* obtained agreed in properties with the hydrocarbon prepared by the action of alcoholic potash on the bromohexylene. The hydrocarbon is a clear, refractive liquid, having the usual odour of the hydrocarbons of the $C_nH_{2n-2}$ series; it boils at 71—73°, and gives no precipitate with ammoniacal cuprous chloride or silver nitrate; its sp. gr. at 0°/0° is 0·7350. Evidence that the hydrocarbon is not methylisopropylacetylene was obtained by submitting it to the action of hypochlorous acid, when no α-dichloroketone was formed (compare Faworsky, Abstr., 1895, i, 496). By brominating the hydrocarbon in the manner described at the beginning of this abstract, a hexylenic dibromide is obtained, which is probably

$$CMe_2Br{\cdot}CH{:}CHMe,$$

since it yields no glycol or unsaturated monobromide when heated with potassium carbonate. This dibromide is a colourless liquid, which boils at 78—79°, and has a sp. gr. at 0°/0° of 1·5878.

*Methylisopropylacetylene* was prepared from methyl isobutyl ketone by treatment with phosphorus pentachloride, and heating the product with alcoholic potash (compare Faworsky, Abstr., 1888, 798). It boils at 71—72·5°; its sp. gr. at 0°/0° is 0·7321; it gives no precipitate with ammoniacal cuprous chloride or silver nitrate. When brominated, it takes up only one atom of bromine; the *monobromide* formed, either $CHMe_2{\cdot}CBr{:}CHMe$ or $CHMe_2{\cdot}CH{:}CMeBr$, is a clear liquid, boiling at 128—131°, and insoluble in water and in potassium carbonate solution.

The author hopes that this difference between the behaviour of trimethylisoallylene and methylisopropylacetylene towards bromine may prove to be a general one between trisubstituted isoallylenes and disubstituted isoallylenes; his present researches are in this direction.

A. G. B.

**Mercuric Oxycyanide.** By LEONCE BARTHE (*J. Pharm.*, 1896, [6], 182—184).—Dorvault's mercuric oxycyanide, $Hg(CN)_2,HgO$, is prepared by dissolving the yellow oxide (22 grams) in a solution consisting of mercuric cyanide (100 grams), and water (1500 grams); the temperature is not allowed to exceed 70°, and hydrogen cyanide is evolved. The oxycyanide requires more than 1000 parts of water to dissolve it, and the solution rapidly attacks nickel and steel. Ditte has described a second oxycyanide, $3Hg(CN)_2,HgO$; it is practically identical with the pharmaceutical preparations which contain about 80·6 per cent. of mercuric cyanide; these readily dissolve in 200 parts of water, but nickel and steel articles placed in the solution become covered with mercury and mercuric oxide in less than 20 minutes, and hydrogen cyanide is evolved. Both these compounds are quite unsuitable for surgical purposes. J. B. T.

**Synthesis of Ethylic Alcohol.** By NIKODEMO CARO (*Chem. Centr.*, 1895, ii, 437; from *Chem. Ind.*, 1895, 226).—Ethylidenic iodide is formed by passing acetylene, from calcium carbide through three Woulff's bottles containing concentrated hydriodic acid, it boils at 175°, "in a vacuum"; the yield is 55—57 per cent. When treated with potash, the iodide is converted into acetylene, and acetaldehyde, the latter is then further changed into alcohol (45 per cent.) and acetic acid. With moist silver oxide, acetylene is formed in traces only, but acetic acid is produced and the yield of alcohol is 90 per cent. When heated with water in a sealed tube at 130—150°, the iodide yields aldehyde, ethylic iodide, and hydriodic acid, but in presence of zinc oxide and zinc dust, alcohol is formed, the yield being 70 per cent. J. B. T.

**Production of Alcohol from Cellulose and Wood.** By E. SIMONSEN (*Bied. Centr.*, 1896, **25**, 47—50; from *Norsk. teknisk. Tidsskr.*, 1895, 65—80).—The results of experiments on the production of sugar from sulphite cellulose showed that the best results are obtained when the following amounts of substances are employed: water 1080 c.c., cellulose 40 grams (or 27 : 1) with sulphuric acid 0·45—0·60 per cent. At a pressure of 8 or 6 atmospheres, the amount of sugar obtained was 45 per cent. of the weight of cellulose. Oxalic acid gave a much smaller yield than sulphuric acid. As regards the length of time of digestion, 20·1 per cent. of sugar was produced in 15 minutes, increasing to 42·7 per cent. with 1½ hour, and diminishing to 35 per cent. after 3 hours' digestion. The introduction of chloroform, by means of which the high pressure was obtained at a lower temperature, caused a great reduction in the amount of sugar produced, indicating that temperature and not pressure is the more essential factor. Besides sugar, a considerable quantity of an acid substance is formed. The sugar seems to be *d*-glucose, but when fermented, yields about 20 per cent. less alcohol than is required by theory.

In the production of sugar from wood shavings (pine) the following conditions were found to give the best results (22·5 per cent.): digestion for 1¼ hour with 0·5 per cent. sulphuric acid, (5 parts) at a pressure of 9 atmos. With acid of over 1 per cent., much less sugar was obtained. In the case of wood, as with cellulose, an acid was produced along with the sugar, and the quantity of this acid was greater the more sulphuric acid was employed; but the increased production of acid did not seem to take place at the expense of the sugar.

The lignin of the wood does not seem to be attacked, sugar being produced from the cellulose alone. The sugar, when fermented, yielded 64 per cent. of alcohol. Wood shavings yield 6·5 per cent. of alcohol. N. H. J. M.

**Bromo-Derivatives of Tricarbon Nuclei.** By ROBERT LESPIEAU (*Bull. Soc. Chim.*, 1896, [3], **13**, 629—632).—1 : 2 : 3-Tribromopropene, $CHBr\colon CBr\cdot CH_2Br$, (Abstr., 1893, i, 1) is a colourless liquid, the vapour of which is irritating to the eyes. It boils at 89—90° (10 mm.), and at 110—112° (20 mm.), and is converted by potash into 1 : 3-*dibromopropine*, $CBr\colon C\cdot CH_2Br$, a colourless liquid, having a very penetrating odour, and boiling at 52—55° (15 mm.). 1 : 3 : 3-*Tribromopropaneoxymethane*, $CH_2Br\cdot CBr_2\cdot CH_2\cdot OMe$, obtained by brominating 2-bromopropeneoxymethane, $CH_2\colon CBr\cdot CH_2O\cdot Me$, is a colourless liquid resembling camphor in odour; it boils at 118—119° (35 mm.) and solidifies in a mixture of solid carbonic anhydride and ether; sp. gr. = 2·229 at 0°. 1 : 2-*Dibromopropeneoxymethane*, $CHBr\colon CBr\cdot CH_2\cdot OMe$, obtained from the preceding compound by the action of sodium methoxide in methyl alcoholic solution, is a colourless liquid of ethereal odour; it boils at 175—177° (745 mm.), and at the same time decomposes slightly; sp. gr. = 1·903 at 0°. It is converted by zinc dust in alcoholic solution into a *propineoxymethane*, $CH\colon C\cdot CH_2\cdot OMe$, but takes up bromine only very slowly, probably forming an additive compound. 1-*bromopropineoxymethane*, $CBr\colon C\cdot CH_2\cdot OMe$, is obtained by the regulated action of dry potash on dibromopropyleneoxymethane. It is a colourless, very volatile liquid, burning with a smoky flame, and boiling at 40° (20 mm.) or 125—126° (740 mm.). JN. W.

**Isopropylic Hydrogen Sulphate.** By LEOPOLD SPIEGEL (*Chem. Zeit.*, 1895, **19**, 1423).—The acid obtained by Dobrin by acting on cardole with concentrated sulphuric acid, has the composition $C_3H_7SO_4H$; it is not identical with propylic hydrogen sulphate, and must therefore be isopropylic hydrogen sulphate. The latter compound, hitherto held to be incapable of existence, has been obtained by the author, in the form of its barium salt, by the following process.

Isopropylic alcohol is added gradually to sulphuric acid, both being ice cold, and the mixture poured into about 30 times its weight of ice-cold water. The solution is neutralised with barium carbonate, and the barium sulphate and excess of carbonate separated in the usual manner. *Isopropylic barium sulphate*, forms transparent crystals; it dissolves readily in water, and when heated at 85°, darkens and gives off the characteristic odour of the salt from cardole, barium sulphate being produced. The crystals on exposure to air become opaque, those of the normal propyl salt remaining transparent under the same conditions. A. L.

**Active Amyl Compounds.** By IDA WELT (*Ann. Chim. Phys.*, 1895, [7], **6**, 115—144).—The first portion of the paper contains results which have already been published (compare Abstr., 1895, i, 203 and ii, 97).

*Amylic phenylic ether*, $C_5H_{11}\cdot OPh$, is obtained by heating dry sodium phenoxide with amylic iodide for about seven hours, it has a sp. gr. = 0·9331 at 17°, a specific rotatory power $[\alpha]_D = +4·01$ at 17°, and its molecular refraction = 51·55 (theory 51·13).

*Amylic paratolylic ether*, sp. gr. = 0·9408 at 17°, sp. rotatory power $[\alpha]_D = +4·26$ at 19°, and molecular refraction = 55·59 (theory 55·73).

*Amylic orthotolylic ether*, sp. gr. = 0·9839 at 20°, sp. rotatory power $[\alpha]_D + 3·86$ at 20°, and molecular refraction = 54·03.

*Amylic metatolylic ether*, sp. gr. = 0·9422 at 22°, sp. rotatory power $[\alpha]_D = +3·93$ at 22°, molecular refraction = 55·85.

*Amylic thymylic ether*, sp. gr. = 0·934 at 18°, sp. rotatory power $[\alpha]_D = +4·17$ at 18°, molecular refraction = 69·96 (theory 69·54).

*Amylic carvacrylic ether*, $C_5H_{11}\cdot O\cdot C_6H_3MePr$, sp. gr. = 0·955 at 19°, sp. rotatory power $[\alpha]_D = +4·0$ at 19°, and molecular refraction = 69·72.

From these and previous results, it follows that the amylic aromatic ethers have much higher rotatory powers than the amylic ethers of the fatty series. The author also points out that the oxides which contain a methyl group in the para-position relatively to the $O\cdot C_5H_{11}$ group have higher rotatory powers than the isomeric oxides which contain the methyl group in the ortho- or meta-position.

J. J. S.

**Formation of Pinacolin from Calcium Isobutyrate.** By CARL GLÜCKSMANN (*Monatsh.*, 1895, **16**, 897—905).—The author has repeated the experiments of Barbaglia and Gucci (Abstr., 1881, 35), on the decomposition by heat of calcium isobutyrate, and has succeeded in isolating from the distillate a substance of the formula $C_6H_{12}O$; it is an oil, boiling at 114—116° (uncorr.); it has ketonic characters, dissolving in solutions of sodium hydrogen sulphite with development of heat. When oxidised with alkaline potassium permanganate, it yields oxalic and isobutyric acids, no appreciable amount of any ketonic substance being formed. It is, therefore, either methyl isobutyl ketone or ethyl isopropyl ketone, and not pinacolin.

Pinacolin may be detected with certainty, even when in small quantity, by means of the trimethylpyruvic acid, which it yields on oxidation. As the latter compound can not be detected in the oxidation products of the oils obtained in the above decomposition, the non-production of pinacolin during the latter is certain. A. L.

**Properties of Dichlorhydrin.** By HUGO FLEMMING (*Chem. Zeit.*, 1895, **19**, 1550).—Dichlorhydrin destroys india-rubber and cork stoppers, and appears to have extraordinary solvent powers, dissolving all resins; thus amber dissolves in about 10 times its weight of the liquid, whilst copals seem to dissolve in all proportions, the solutions, however, cannot be filtered. This property is shown in a less degree by epichlorhydrin.

Pure dichlorhydrin boils at 176° under 765 mm. pressure, its sp. gr. = 1·364 at 15°. A. L.

**Multirotation of Reducing Sugars and of Isodulcitol.** By CHARLES TANRET (*Compt. rend.*, 1896, **122**, 86—87).—$\beta$-Isodulcitol can be obtained in crystals in two ways: (*a*) 1 part of isodulcitol is dissolved in 0·5 part of water, and the warm solution is mixed with 5 parts of absolute alcohol and then with 9 parts of ether; $\alpha$-isodulcitol is precipitated, but on adding more ether, the $\beta$-derivative is obtained in slender prismatic needles; (*b*) a solution of ordinary isodulcitol is concentrated on a water bath until it forms a thick syrup, and fragments of the $\beta$-compound obtained by the first process are added from time to time with constant agitation; $\beta$-isodulcitol separates as a crystalline anhydrous powder. The rotatory power of the product (*a*) is at first $[\alpha]_D = +10·29°$, and of product (*b*) +12°, but after an hour these numbers become +9·6° and +10° respectively.

The $\beta$-isodulcitol contains a third modification, $\gamma$-isodulcitol, which can be produced by heating at 90° the $\beta$-isodulcitol obtained by method (*a*). When first dissolved in water, its specific rotatory power is +20°, but sinks to +10° after an hour.

Anhydrous isodulcitol softens at 105°, and melts distinctly at 108°; when exposed to moist air, it combines with water and is partially reconverted into $\alpha$-isodulcitol. C. H. B.

**Dichloralglucose and Chloralglucosan.** By JEAN MEUNIER (*Compt. rend.*, 1896, **122**, 142—144).—85 grams of chloral hydrate and 130 c.c. of sulphuric acid of 60° are triturated together, 100 grams of finely powdered glucose is added, and trituration continued. After a few minutes, the product is thrown into water, and the insoluble portion, after being well washed, is crystallised from boiling alcohol. It contains (1) chloralglucose, or chloralose, soluble in cold alcohol, and crystallising in needles which melt at 185—187°; (2) *dichloralglucose*, $C_6H_{10}O_4(C_2Cl_3O)_2$, this crystallises in white needles, which melt at about 225°, dissolve in 300 parts of alcohol, and in 45 parts of ether at about 20°; it is not decomposed by acids; (3) *chloralglucosan*, $C_6H_9O_4,C_2Cl_3O$, which forms nacreous lamellæ, melting at about 225°, insoluble in water or in cold alcohol, but soluble in boiling alcohol. It requires 1,000 parts of ether for dissolution, and is not attacked by acids.

Dichloralglucose and chloralglucosan are reduced by zinc in presence of boiling acetic acid, and the products are under investigation. C. H. B.

**Hydrolysis and Estimation of Sugar.** By JAMES O'SULLIVAN (*J. Soc. Chem. Ind.*, 1895, **14**, 555—556).—The author has proved that a 10 per cent. solution of cane sugar, containing 4 per cent. of sulphuric acid by volume, was completely inverted at the ordinary temperature in about seven days.

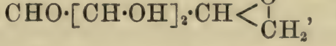
The solution was then most carefully neutralised with barium carbonate and the copper-reducing power was taken. The result confirmed the generally accepted idea that the copper oxide, multiplied by 0·4535, represents the amount of invert sugar. L. DE K.

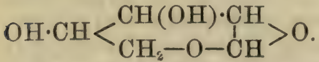
**Lintner's Isomaltose.** By CHRISTOPH ULRICH (*Chem. Zeit.*, 1895, **19**, 1523).—The author has repeated, under similar conditions, the work of Lintner and Düll (compare Abstr., 1893, i, 5) on the action of diastase on starch. All the fractions of the product whose rotations approached that of Lintner's isomaltose, $[\alpha]_D = +140$, were mixed and refractionated as before, and the process repeated. From the final fractions, with the above specific rotation, osazones were prepared and fractionally crystallised, when they were found to melt most indefinitely, but in no case were they completely melted below 159°; as a rule, they melted between 165° and 175°, whilst the osazone described by Lintner melted at 150—153°. The above osazone behaved, on recrystallisation, like maltosazone, and had nearly the same rotation; the author concludes that it is identical with that substance.

Crystals, deposited from various fractions of the syrup, were found in all cases to be maltose, whilst the accompanying syrup gave some quantity of glucosazone on treatment with phenylhydrazine.

From these results, the author concludes that the incomplete action of malt extract on starch at 70°, leads to the production, not of isomaltose, but of ordinary maltose (compare Ling and Baker, Trans., 1895, 702, 739; Brown and Morris, *ibid.*, 709). A. L.

**Ethereal Derivatives of Wood Gum [Xylan] and of Xylose.** By RICHARD BADER (*Chem. Zeit.*, 1895, **19**, 55—56 and 78).—*Acetylxylan*, $C_5H_7AcO_4$, is obtained when finely powdered wood-gum, which has been air-dried, is treated with excess of acetic chloride. After warming for a few minutes on the water bath, the mixture is cooled, diluted with acetic acid, and then precipitated with an excess of absolute alcohol. The dry acetyl derivative forms a yellowish-brown, amorphous powder, which is but sparingly soluble in boiling acetic acid, and can only be further purified with great difficulty.

*Diacetylxylan*, $C_5H_6Ac_2O_4$, is formed when the monacetyl derivative is intimately mixed with a considerable excess of acetic anhydride and then heated in sealed tubes at 140—150°. It resembles the monacetyl compound in appearance, and is also very sparingly soluble in most solvents. The author has found it impossible to introduce more than two acetyl groups into the xylan molecule, a property which agrees with either of the two constitutions for xylan suggested by Tollens, namely,  $CHO\cdot[CH\cdot OH]_2\cdot CH<\begin{matrix}O\\|\\CH_2\end{matrix}$, or



$$OH\cdot CH<\begin{matrix}CH(OH)\cdot CH\\ | \\ CH_2-O-CH\end{matrix}>O.$$

*Benzoylxylan* is best prepared by Baumann's method; after washing with water and boiling alcohol, it forms a brownish, amorphous mass, and is only sparingly soluble in boiling acetic acid. A dibenzoyl derivative could not be obtained.

A mixture of xylan *mono-* and *di-nitrate* is obtained when dried wood gum is added to cold nitric acid (sp. gr. 1·525), and the mixture is poured into cold water. The author has found it impossible to separate the two, and can find no trace of oxalic acid among the products of the action of concentrated nitric acid on xylan.

Stone's tetracetylxylose (Abstr., 1895, i, 104) may also be obtained by heating xylose with an excess of acetic anhydride for 2½—3 hours in a sealed tube at 140°. It forms small needles and melts at 126° (Stone, 123·5—124·5°). In attempting to prepare the tetracetyl compound, the author, on one occasion, obtained quite a different result. The product, when boiled with water, yielded a strong smell of turpentine oil, and, on distillation with superheated steam, a small quantity of a colourless oil passed over, and a brown resin was left. The quantities of these two products were too small for complete investigation, and the author could not obtain them in any subsequent experiment.

Pure xylose, when added to concentrated nitric acid (sp. gr. 1·48), yields no trace of oxalic acid, the anhydride of trihydroxyglutaric acid (probably the anhydride of Fischer's acid, compare Abstr., 1891, 177) apparently being formed.

J. J. S.

**Diastatic Resolution of Starch.** By HANS MITTELMEIER (*Chem. Centr.*, 1895, ii, 163; from *Wchschr. Brauereï*, **12**, 480—482).—Unlike Lintner, the author has failed to obtain maltose from its isomerides by the action of diastase. He regards the diastatic resolution of starch as occurring in two phases; in the first, a small portion of the starch is rapidly converted into amylo-, achroo-, and erythro-dextrins and sugar, but these dextrins are not identical with those formed later; the former are termed primary, the latter secondary, dextrins.

*Primary erythrodextrin* is deposited from water in an insoluble state, $[\alpha]_D$ = about +170°; it is soluble in phenylhydrazine, reduces alkaline copper solution, and yields dextrose and maltose when treated with diastase. *Primary achroodextrin* has also been isolated. The sugar obtained from the primary dextrins yields, with phenylhydrazine, maltosazone; that from the secondary dextrins, an oily osazone, which softens at 120°, melts at 145—148°, and is probably derived from a new biose, for which the term *metamaltose* is suggested.

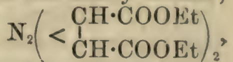
J. B. T.

**Action of the Halogens on the Methylamines.** By IRA REMSEN and JAMES F. NORRIS (*Amer. Chem. J.*, 1896, **18**, 90—95).—When dry trimethylamine is passed into ice-cold bromine, it is absorbed, giving a yellow precipitate of *trimethylamine dibromide*, $NMe_3Br_2$. The following method of preparation is more convenient. Trimethylamine hydrobromide (1 mol.), with just enough concentrated hydrobromic acid to dissolve it on heating, is mixed with bromine (1 mol.) and heated. On cooling, light yellow plates crystallise out, which, on recrystallisation from alcohol, are obtained as stout, prismatic needles. The salt is instantly decomposed by water, with liberation of just half the bromine. By passing trimethylamine into iodine dissolved in absolute alcohol, the *diiodide*, $NMe_3I_2$, is obtained as a light yellow precipitate, which gradually changes to a dark brown, viscous liquid. Hydrochloric acid decomposes it immediately, with liberation of iodine, but water does not affect it until heated, when much more than half the iodine is set free, probably owing to the action of the hydriodic acid formed. The *dichloride* seems to be obtained by the action of dry chlorine on dry trimethylamine. It is a white solid, is very hygroscopic, has a strong odour of chlorine, is very easily decomposed by moist air, and could not be analysed. With excess of chlorine, trimethylamine burns and deposits soot. The preparation and properties of *dimethylamine dibromide* are similar to those of the trimethylamine compound. Compounds containing two different halogen atoms were also obtained. Thus, the chloride of either di- or tri-methylamine gives with bromine a compound containing both bromine and chlorine, and the chlorides and bromides of both amines yield, with iodine, compounds which give up iodine in contact with water. Methylamine could not be made to yield either bromine or iodine substitution products by methods analogous to those described. A. E.

**New Method of preparing Aliphatic Diazo-compounds.** By Wilhelm Traube (*Ber.*, 1896, **29**, 667—670).—When the sodium or lead salt of an aliphatic isonitramic acid (Abstr., 1895, i, 502) is reduced with sodium amalgam at 0°, the sodium salt of a diazo-acid is formed as the chief product of the action; some hydrazido-acid (compare this vol., i, 340) is also formed at the same time. Thus, sodium isonitramineacetate, $HO_2N_2\cdot CH_2\cdot COONa$, yields sodium diazoacetate, $N_2:CH\cdot COONa$, and, by evaporating the resulting strongly alkaline solution at 30—40° under diminished pressure, this salt can be obtained as a yellow, crystalline substance, which explodes when heated, but not when struck; the yield is more than 50 per cent. of the theoretical. Neither the acid itself, nor its salts with heavy metals, are stable; they decompose at once in aqueous solution with evolution of nitrogen.

In the case of the homologues, it was not possible to isolate salts of the diazo-acids; solutions, however, were obtained which evolved nitrogen when acidified, and doubtless contained such salts.

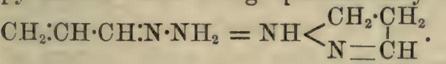
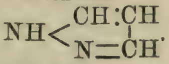
C. F. B.

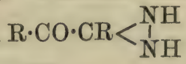
**Hydrazine, Azoimide, and Aliphatic Diazo-derivatives.** By Theodor Curtius (*Ber.*, 1896, **29**, 759—783).—A lecture delivered to the German Chemical Society. The discovery of ethylic amidoacetate hydrochloride rendered it necessary to show that the ethylic group was linked to carboxyl, and not to nitrogen; proof of this is afforded by the action of nitrous acid, which results in the formation of ethylic diazoacetate; the synthesis of methyleneamidoacetonitrile, $CH_2:N\cdot CH_2\cdot CN$, from formaldehyde and ammonium cyanide, and its conversion into formaldehyde and amidoacetic acid, rendered the latter compound easily accessible. Ethereal salts of diazo-acids may be prepared directly from albuminous matter, such as glue, cheese, or old woollen fibres, by the successive action of alcoholic hydrogen chloride and sodium nitrite, and they may be immediately converted into hydrazine; in this manner, it is possible, in the course of a few minutes, to demonstrate the presence of amido-groups in egg-albumin. Diazoacetic acid is only known in the form of its amide, alkali, and ethereal salts, but the ethylic salt forms salts with the heavy metals; when heated, it yields ethylic azinesuccinate,  $N_2\left(<\begin{matrix}CH\cdot COOEt\\ | \\ CH\cdot COOEt\end{matrix}\right)_2$, which readily decomposes, on further heating, into nitrogen and fumaric acid. Ethylic diazosuccinate yields an isomeric azinesuccinate, probably the asymmetric compound $N_2[C(COOEt)\cdot CH_2\cdot COOEt]_2$; neither of these azines give hydrazine when hydrolysed.

Diazoacetic acid, like diazomethane, reacts with almost all substances, including organic and mineral acids, haloïds, water, alcohols, phenols, hydrocarbons, aniline, and benzaldehyde; in all these cases, nitrogen is replaced by hydrogen and a radicle: thus, with water and alcohol, respectively, glycollic acid and ethylglycollic acid are formed. With dilute alkali, ethylic diazoacetate yields the normal salt, which, when acidified, is converted into glycollic acid, but, with concentrated alkali, triazoacetic acid, $COOH\cdot CH<\begin{array}{l}N_2\cdot CH(COOH)\\N_2\cdot CH(COOH)\end{array}>N_2$, is formed, and this, when hydrolysed by means of dilute mineral acids, is converted into hydrazine and oxalic acid, or carbonic anhydride and formic acid; hydrazine is also formed by the reduction of azoacetic acid to hydrazineacetic acid, $COOH\cdot C<\begin{array}{c}NH\\|\\NH\end{array}$, and the hydrolysis of this to glyoxalic acid; von Pechmann's synthesis of it from diazoacetic acid and alkali sulphite, and Buchner's from ethylic diazoacetate and salts of unsaturated acids, such as ethylic fumarate, are analogous. Thiele's method, which is of much practical importance, consists in reducing nitroguanidine prepared from potassium ferrocyanide, to amidoguanidine, which is then hydrolysed to hydrazine, carbonic anhydride, and ammonia.

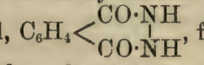
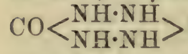
Hydrazine is characterised by its powerful reducing action, many salts which yield the lower oxides with other reducing agents are converted into metals by hydrazine; the haloïds and sulphur are converted into hydrogen compounds, and zinc slowly dissolves, forming a crystalline salt. Although hydrazine is apparently symmetrical, its derivatives of the type $N_2H_6'' = \overset{v}{N}H_3\cdot\overset{v}{N}H_3$, such as $N_2H_4,2H_2O$ and $N_2H_4,2HCl$, are highly unstable, whilst those of the type $N_2H_5 = \overset{III}{N}H_2\cdot\overset{v}{N}H_3$, such as $N_2H_4,HCl$ and $N_2H_4,H_2O$, are stable; the sulphate is an exception, it does not form an alum, but yields anhydrous double salts, $(N_2H_5)_2SO_4,R''SO_4$ ($R''$ = Cu, Ni, Co, Fe, Mn, Cd, Zn, but not Mg), but the double chlorides $N_2H_5Cl,R''Cl_2$ and $(N_2H_5Cl)_2,R''Cl_2$ correspond with the ammonium derivatives; thus, the compound $NiSO_4,6NH_3$ has its analogue in $NiSO_4,3N_2H_4$, which, like nickel carbonyl, indicates the possible octovalency of nickel.

Azoimide is formed from nitrous anhydride and hydrazine; Thiele obtained it from amidoguanidine in a similar manner, and Wislicenus from nitrous oxide and ammonia in presence of sodium. The author's method consists in converting an insoluble amide into a hydrazide, $R\cdot CO\cdot NH\cdot NH_2$, which is then transformed, by means of nitrous acid, into the azoimide $RCON_3$; this, when hydrolysed with alcoholic ammonia, regenerates the amide and forms ammonium azoimide, which may be employed with perfect safety. Azoimide itself was only obtained anhydrous on one occasion; it has a powerful smell, and boils at about the same temperature as ether; subsequent attempts to isolate it were unsuccessful, as it always exploded with great violence at the ordinary temperature. The ammonium salt is employed as an explosive, but with care it may be sublimed like ammonium chloride. The hydrazine salt, $N_2H_5N_3$, forms large, hygroscopic crystals, which burn quietly, like guncotton. In general chemical behaviour, the group $N_3$ resembles a haloïd atom. Hydrazine hydrate reacts with ethylic iodide, like potash, giving ethylene and hydrazine iodide; its constitution is shown by the production of 1 : 2 : 4-dinitrophenylhydrazine from 1 : 2 : 4-dinitraniline and from 1 : 2 : 4-dinitrobromobenzene.

The aldehyde hydrazones are unsymmetrical, $R{\cdot}CHN{\cdot}NH_2$, and are readily converted into azines, $RCH{:}N{\cdot}N{:}CHR$, which, when reduced, yield hydrazines, analogous to hydrazobenzene, but these do not yield azo-derivatives, $R{\cdot}CH_2{\cdot}N{:}N{\cdot}CH_2R$, by oxidation. The ketohydrazones and azines resemble the aldehyde derivatives, and, if the ketazines contain the group $-CMe{:}N-$, they readily yield pyrazoline derivatives, pyrazoline itself being spontaneously formed from acrylhydrazone,  $CH_2{:}CH{\cdot}CH{:}N{\cdot}NH_2 = NH{<}\begin{matrix}CH_2{\cdot}CH_2\\ N{=}CH\end{matrix}$. By the action of bromine, pyrazoline yields pyrazole,  $NH{<}\begin{matrix}CH{:}CH\\ N{=}CH\end{matrix}$.

Orthoketones and ethereal salts of $\alpha$-ketonic acids react with hydrazine to form hydrazi-derivatives,  $R{\cdot}CO{\cdot}CR{<}\begin{matrix}NH\\ NH\end{matrix}$ or

$$\begin{matrix}NH\\ NH\end{matrix}{>}CR{\cdot}CR{<}\begin{matrix}NH\\ NH\end{matrix},$$

which, on oxidation, yield azo-compounds, whilst the hydrazones give unstable tetrazones, then ketazines and nitrogen; the hydrazi-derivatives do not form ketazines when heated, but nitrogen is eliminated; thus, hydrazibenzil is converted into deoxybenzoïn. Ethereal salts of $\beta$- and $\gamma$-ketonic acids react with hydrazine as with phenylhydrazine, except that the resulting compounds usually change spontaneously into derivatives of pyrazolone and pyridazinone. von Rothenburg's synthesis of pyrazolone from hydrazine and ethylic propiolate, and of pyrazolidone from hydrazine and acrylic acid, are referred to, also the compound,  $C_6H_4{<}\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}$, from phthalic anhydride. Hydrazine reacts with ethereal salts to form acid hydrazides, $R{\cdot}CO{\cdot}NH{\cdot}NH_2$. Amides, acid chlorides, and azoimides react like the ethereal salts; by the action of iodine, or of a second molecule of the ethereal salt, the hydrazides are converted into symmetrical secondary hydrazines, $R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}COR$; the hydrazides condense with aldehydes, forming tertiary hydrazines, $RCO{\cdot}NH{\cdot}N{:}CHR$, which are entirely different from the aldazines (see above). With nitrous acid, the hydrazides are converted into azoimides, $R{\cdot}CON_3$ (see above), which closely resemble the acid chlorides and bromides, except that those of the aliphatic series are explosive; with diazo-salts, the same change takes place, but buzylene derivatives are formed as intermediate compounds: thus, benzhydrazide and diazobenzene yield phenylbenzoylbuzylene, $COPh{\cdot}NH{\cdot}NH{\cdot}N{:}NPh$; this, according to circumstances, gives benzazoimide, $Ph\cdot CON_3$, and aniline, or benzamide and phenylazoimide, $PhN_3$. The azoimides are converted, by the action of water, into nitrogen, carbonic anhydride, and carbamide derivatives; alcohol acts in a similar manner, but yields urethanes instead of carbonic anhydride and carbamides. These reactions furnish a ready means of replacing carboxyl by the amido-group, the steps being, acid—ethylic salt—hydrazide—azoimide—urethane—amine. The hydrazides and azoimides react to form semicarbazides, and nitrogen derivatives of "prozane," $NH_2\cdot NH\cdot NH_2$, are not formed, as might have been expected. The azoimide and hydrazide derivatives of carbonic acid are of special interest; they include semicarbazide, $NH_2\cdot CO\cdot NH\cdot NH_2$, dicarbamide,  $CO<\begin{matrix}NH\cdot NH\\NH\cdot NH\end{matrix}>CO$, an energetic acid, and carbazoimide, $CON_6$, which is highly explosive. J. B. T.

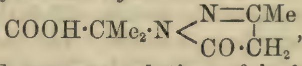
**Hydrazido-acids.** By WILHELM TRAUBE and G. G. LONGINESCU (*Ber.*, 1896, **29**, 670—675).—When an isonitramic acid is reduced with sodium amalgam at 0° (compare this vol., i, 337), there is formed, in addition to the salt of the diazo-acid, a hydrazido-acid, in amount equal to about 5 per cent. of that theoretically possible. Thus, isonitraminepropionic acid, $HO_2N_2\cdot CHMe\cdot COOH$, yields hydrazidopropionic acid, $NH_2\cdot NH\cdot CHMe\cdot COOH$. This acid is isolated by acidifying the solution, when the diazo-acid is destroyed, and then forming the benzylidene derivative of the hydrazido-acid by adding benzaldehyde until the solution no longer reduces Fehling's solution. This derivative sometimes separates out in crystals, but usually has to be extracted with ether; it is readily decomposed by steam distillation, or by warming with dilute acid, into benzaldehyde and the hydrazido-acid, the latter being obtained when the residue is evaporated. These hydrazido-acids reduce Fehling's solution, and form salts with acids, but not with bases.

Hydrazidoacetic acid could not be isolated. *Hydrazidopropionic acid* melts at 180°, its *benzylidene derivative* at 106°, its *hydrochloride* at 155°. It condenses with ethylic acetoacetate, forming crystals which lose yet a molecule of alcohol when evaporated with water, and form methylpyrazolonepropionic acid, melting at 215°. *Hydrazidobutyric acid* melts at 208°, its *benzylidene derivative* at 125°; *hydrazidovaleric acid* at 215°, its *benzylidene derivative* at 116°; *hydrazidobenzylacetic acid* at 196°, its *benzylidene* and *salicylidene derivatives* at 153° and 134° respectively. C. F. B.

**Hydrazine Derivatives of Isobutyric acid.** By JOHANNES THIELE and KARL HEUSER (*Annalen*, 1896, **290**, 1—43).—The authors' improvement in the preparation of semicarbazide (this vol., i, 208) has enabled them to investigate the hydrazine derivatives of isobutyric acid.

*Benzylidenehydrazidoisobutyric acid*, $CHPh\colon N\cdot NH\cdot CMe_2\cdot COOH$, is obtained by hydrolysing carbonamidohydrazoisobutyronitrile, which Thiele and Stange obtained from acetonesemicarbazone by the action of hydrogen cyanide (Abstr., 1895, i, 252), and treating the product with benzaldehyde; it is insoluble in water, and crystallises from alcohol in white needles melting at 144—145° The *silver* salt dissolves with difficulty, and rapidly becomes black.

*Hydrazidoisobutyric acid*, $NH_2{\cdot}NH{\cdot}CMe_2{\cdot}COOH$, is formed from the preceding compound on submitting it to the influence of a powerful current of steam; it dissolves readily in water, but is insoluble in alcohol or ether, and melts and decomposes at 237°. The acid reduces cold Fehling's solution and an ammoniacal silver solution, and yields hydrazine when treated with boiling acids, although caustic soda does not produce this effect; bromine water and ferric chloride oxidise the substance, the former agent liberating the quantitative amount of nitrogen, along with carbonic anhydride. The *hydrochloride* crystallises from water in rosettes of needles, and melts at 156—157°, the *sulphate* melts and decomposes at 189°, and the *nitrate* crystallises in leaflets and melts at 146°; the *ethylic* salt boils at 93—95° under a pressure of 13 mm., and yields a crystalline *hydrochloride*.

*3-Methylpyrazoloneisobutyric acid*,  $COOH{\cdot}CMe_2{\cdot}N{<}\begin{array}{l}N{=}CMe\\ \quad\;\;|\\ CO{\cdot}CH_2\end{array}$, is obtained by agitating a concentrated aqueous solution of hydrazidoisobutyric acid with ethylic acetoacetate; it crystallises from hot water in yellowish needles, and melts at 263°. A red coloration is developed with ferric chloride.

The *mononitrile* of hydrazodiisobutyric acid (*hydrazoisobutyronitrilic acid*), $COOH{\cdot}CMe_2{\cdot}NH{\cdot}NH{\cdot}CMe_2{\cdot}CN$, is formed when concentrated aqueous solutions of hydrazidoisobutyric acid and potassium cyanide are agitated with acetone (1 mol.), and after 24 hours treated with the calculated quantity of hydrochloric acid; it melts at 100°, is readily soluble in alcohol and ether, dissolves sparingly in petroleum, and reduces ammoniacal silver and Fehling's solution.

The *dinitrile*, $CN{\cdot}CMe_2{\cdot}NH{\cdot}NH{\cdot}CMe_2{\cdot}CN$, is obtained by agitating hydrazine sulphate and potassium cyanide (2 mols.) in concentrated aqueous solution with acetone (2 mols.); it crystallises from ether in lustrous plates, and melts at 92—93°. The *hydrochloride* is amorphous, and loses hydrogen chloride when exposed to air; the *dinitroso*-derivative melts at 43—44°, and yields azo-isobutyronitrile (see below) when heated or exposed to air, nitric oxide being eliminated.

*Hydrazodiisobutyric acid*, $COOH{\cdot}CMe_2{\cdot}NH{\cdot}NH{\cdot}CMe_2{\cdot}COOH$, which is formed on hydrolysing the dinitrile with concentrated hydrochloric acid, crystallises from water in lustrous prisms, melting at 223—224°; the aqueous solution is acidic, and the substance, although a dicarboxylic acid, is monobasic in character. The *ammonium* salt is a lustrous, crystalline powder, and the *silver* salt rapidly becomes black; the *calcium* salt crystallises in needles, and contains $2H_2O$, the *potassium* salt is crystalline, and the *hydrochloride*, which contains $1H_2O$, separates in aggregates of small needles. The *methylic* salt separates from petroleum in long, lustrous prisms, melts at 53—54°, and boils at 216°; the *ethylic* salt boils at 231—233°, and has the sp. gr. = 0·99784 at 23°/4°. When hydrazodiisobutyric acid is heated at 200° in a vacuum, it sublimes in crystals which melt at 223—224°, but, under atmospheric pressure, ammonia and carbonic anhydride are evolved, along with inflammable gas which reduces an ammoniacal silver solution; in a sealed tube at 270°, the acid gives rise to a crystalline *compound* which has the formula $C_8H_{14}N_2O_2$, and does not melt at 250°.

*Azodiisobutyronitrile*, $CH\cdot CMe_2\cdot N{:}N\cdot CMe_2\cdot CN$, is produced on oxidising hydrazodiisobutyronitrile with bromine water, and crystallises from ether in long, silvery prisms, which melt and evolve gas at 105—106°; on the application of heat, the whole of the azoic nitrogen is liberated quantitatively. The *hydrochloride* of azodiisobutyric acid imidomethyl ether, $N_2[CMe_2\cdot C(OEt){:}NH,HCl]_2$, is formed when hydrogen chloride acts on azodiisobutyronitrile suspended in methylic alcohol; it melts and decomposes at 133—134°, and loses hydrogen chloride when treated with water. The *hydrochloride* of azodiisobutyric acid imidoethyl ether melts at 106—107°, yielding nitrogen and methylic chloride; the clear, aqueous solution becomes turbid when heated, yielding the ethylic salt of azodiisobutyric acid (see below), and this substance, on the application of heat, yields white prisms which melt at 124°, and probably consist of tetramethylsuccinamide. The *amidoxime* of azodiisobutyric acid, $NH_2\cdot C(NOH)\cdot CMe_2\cdot N{:}N\cdot CMe_2\cdot C(NOH)\cdot NH_2$, is obtained by the action of hydroxylamine on azodiisobutyronitrile; it melts at 154°.

*Ethylic azodiisobutyrate*, $COOEt\cdot CMe_2\cdot N{:}N\cdot CMe_2\cdot COOEt$, is formed by the oxidation of ethylic hydrazodiisobutyrate with bromine water in presence of dilute hydrochloric acid; the yellowish liquid, which has the sp. gr. = 0·9884 at 24·6°/4°, loses its nitrogen quantitatively at 95°. Stannous chloride reduces the salt to ethylic hydrazodiisobutyrate. *Methylic azodiisobutyrate* is obtained by oxidising methylic hydrazodiisobutyrate; it crystallises from light petroleum in large plates, and melts at 33°, nitrogen being eliminated quantitatively above 80°. The *amide* of azodiisobutyric acid is produced by the action of ammonia on the foregoing salts, and crystallises from dilute alcohol in rhombic plates, which melt and decompose at 94—95°; it contains $2H_2O$, which is lost in the exsiccator. The amide crystallises from methylic alcohol in anhydrous plates, and in this condition melts at 104°; when suspended in hot olive oil, the azoic nitrogen is eliminated quantitatively. *Potassium* azodiisobutyrate contains $1H_2O$, softens at 180°, and melts and decomposes at 250°; it is obtained from the methylic and ethylic salts by the action of potash dissolved in methylic alcohol. An aqueous solution of this salt is strongly alkaline, and slowly reduces ammoniacal silver solution when heated; acids induce effervescence, liberating carbonic anhydride, the acetone compound of hydrazidoisobutyric acid being formed at the same time.

*Tetramethylsuccinonitrile*, $CN\cdot CMe_2\cdot CMe_2\cdot CN$, is obtained by treating azodiisobutyronitrile with water heated almost at 100°, nitrogen being eliminated; it crystallises from very dilute alcohol in lustrous, silvery leaflets and prisms, and melts at 169°. When hydrolysed with 80 per cent. sulphuric acid, it yields a mixture of tetramethylsuccinic acid and its anhydride. *Ethylic tetramethylsuccinate*, is formed when ethylic azodiisobutyrate is heated on the water bath; it boils at 218—220°. M. O. F.

**Semicarbazones.** By MAX SCHOLTZ (*Ber.*, 1896, **29**, 610—613).—When the semicarbazones, $CRR'{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, of dimethyl ketone, methyl ethyl ketone, or methyl propyl ketone (the last named melts at 100°) are distilled alone, they yield bis-azimethylenes, $N_2({:}CRR')_2$, and hydrazodicarbonamide, $N_2H_2(CO{\cdot}NH_2)_2$, the latter decomposing for the most part into the imide and ammonia.

Mesityl oxide semicarbazone melts at 156°; when distilled, it does not decompose, but is converted into an isomeride which melts at 129° and boils at 212—213°; simple melting is even sufficient to effect the transformation. C. F. B.

**Inorganic Derivatives of Secondary Aliphatic Amines.** By C. A. AUGUST MICHAELIS and K. LUXEMBOURG (*Ber.*, 1896, **29**, 710—715).—*Chlorophosphines*, $NR_2{\cdot}PCl_2$, are obtained on slowly adding the amine (2 mols.) to phosphorous chloride (1 mol.), cooling meanwhile; they are slowly decomposed by water. *Diethylaminechlorophosphine* boils at 189° under atmospheric, and at 72—75° under 14 mm., pressure; its sp. gr = 1·196 at 15°; *diisobutylaminechlorophosphine* melts at 37—38°, and boils at 115—117° under 16 mm. pressure; *piperidinechlorophosphine* boils at 94—95° under 10 mm. pressure.

*Oxychlorophosphines*, $NR_2{\cdot}POCl_2$, are obtained by adding an ethereal solution of phosphorus oxychloride to a cooled ethereal solution of the amine (2 mols.); they smell either like camphor or like pepper, are only very slowly decomposed by water, and yield ethereal salts with sodium ethoxide or phenoxide, hydrazides with phenylhydrazine, and tertiary phosphine oxides with aromatic amines. *Diethylamineoxychlorophosphine* boils at 100° under 15 mm. pressure; *dipropylamineoxychlorophosphine* boils at 170° under 80 mm. pressure, and its sp. gr. = 1·1799 at 13°, and index of refraction = 1·4653; *diisobutylamineoxychlorophosphine* melts at 54°, and can be distilled under diminished pressure; *diamylamineoxychlorophosphine* boils at 150° under 12 mm. pressure, and its sp. gr. = 1·0804 at 13°.

*Thiochlorophosphines*, $NR_2{\cdot}PSCl_2$, are obtained by heating a mixture of the amine (2 mols.) with phosphorus thiosulphochloride (1 mol.) at 100—120°; they are very stable substances, smell like camphor, and react like the oxychlorophosphines. *Diethylaminethiochlorophosphine* boils at 100° under 15 mm. pressure, and its sp. gr. = 1·105 at 15°; *dipropylaminethiochlorophosphine* boils at 132—134° under 15 mm. pressure, and its sp. gr. = 1·077 at 15°; *diiosbutylaminethiochlorophosphine* melts at 36°, and boils at 150° under 10 mm. pressure; *diamylaminethiochlorophosphine* boils at 160—163° under 10 mm. pressure, and its sp. gr. = 1·0288 at 15°.

*Chlorarsines*, $NR_2{\cdot}AsCl_2$, can be obtained in the same way as the chlorophosphines. *Diisobutylaminechlorarsine* is crystalline, and boils at 125° under 15 mm. pressure.

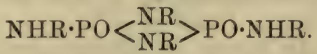
*Chlorosilicines*, $NR_2{\cdot}SiCl_3$, are obtained by the action of the amine (2 mols.) on silicon chloride (1 mol.); they fume in the air, and are slowly decomposed by water. *Diethylaminechlorosilicine* boils at 104° under 80 mm. pressure; *diisobutylaminechlorosilicine* at 120—124° under 30 mm. pressure.

*Chloroborines*, $NR_2{\cdot}BCl_2$, are obtained by treating boron chloride with the amine, cooling meanwhile; they colour the Bunsen flame a vivid green, fume in the air, and are at once decomposed by water. *Diethylaminechloroborine* boils at 140—144° under atmospheric pressure; *dipropylaminechloroborine* at 99° under 45 mm. pressure; and *diisobutylaminechloroborine* at 92—95° under 17 mm. pressure.

In addition to these, compounds such as $NR_2{\cdot}Cl$, $NR_2{\cdot}OH$, &c., are known, so that the imidohydrogen atom of secondary aliphatic amines can be replaced by atoms belonging to very different groups of the periodic system. C. F. B.

**Oxyphosphazo-compounds.** By C. A. AUGUST MICHAELIS and E. SILBERSTEIN (*Ber.*, 1896, **29**, 716—728).—Oxyphosphazo-compounds, $NR{:}PO{\cdot}NHR$, are most conveniently prepared by heating a primary aromatic amine (2 mols.) and phosphorus oxychloride (1 mol.) with enough xylene to make the mass into a paste; they can also be obtained by heating either secondary oxychlorophosphines, $(NHR)_2POCl$, or tertiary phosphine oxides, $(NHR)_3PO$. They are white, sandy powders, occasionally in small crystals, melt at a high temperature, and are insoluble, or only slightly soluble, in the ordinary solvents; from the chemical point of view, they are extremely stable. In analysing them, the carbon had to be determined by oxidation in the wet way; the ordinary method yielded results which were too low. They dissolve in alcoholic sodium ethoxide, or phenol, forming ethyl and phenyl derivatives, probably with the constitution $(NHR)_2PO{\cdot}NR{\cdot}PO(OEt){\cdot}NHR$ (the phenyl compound in some cases has the constitution $OPh{\cdot}PO{:}(NHR)_2$).

In the case of oxyphosphazobenzeneanilide, which was studied in greater detail, the further action of phenol at a higher temperature results in the formation of the phenylic salt, $NHPh{\cdot}PO(OPh)_2$. Heating for six hours with water, alcohol, or dilute aqueous soda, at 150° effects a decomposition into aniline, orthophosphoric acid, and *trianilinephosphine hydroxide*, $(NHPh)_3P(OH)_2$, which melts at 217°. Heating with concentrated sulphuric acid, or with hydrochloric acid in a sealed tube, decomposes it into aniline and phosphoric acid; and on prolonged heating with glacial acetic acid, it yields aniline, orthophosphoric acid, and trianilinephosphine oxide, $(NHPh)_3PO$, the last being also formed when the phosphazo-compound is heated with aniline at a moderate temperature. It is suggested that these oxyphosphazoanilides have in reality double the formula given above, and that their structure is represented by the formula



$$NHR{\cdot}PO{<}{}^{NR}_{NR}{>}PO{\cdot}NHR.$$

The following is a list of the compounds described, with their melting points:—*Oxyphosphazobenzeneanilide*, $NPh{:}PO{\cdot}NHPh$, 357°; *ethylic salt*, 220°; *phenylic salt*, 240°. [A crystallised compound, $(NHPh)_3PO + NH_2Ph$, was incidentally prepared; it melts at 280°.] *Oxyphosphazometachlorobenzenechloranilide*, $C_6H_4Cl{\cdot}N{:}PO{\cdot}NH{\cdot}C_6H_4Cl$, 341°. *Oxyphosphazometabromobenzenebromanilide*,

$$C_6H_4Br{\cdot}N{:}PO{\cdot}NH{\cdot}C_6H_4Br,$$

329°; *ethylic salt*, 203°; forms, with aniline, a compound,

$$NHPh{\cdot}PO(NH{\cdot}C_6H_4Br)_2,$$

165°. The *oxyphosphazo-compounds* of *dichlor-* [$NH_2 : Cl_2 = 1:2:4$], *dibrom-* (335°), *trichlor-* (285°), and *tribrom-aniline* were also prepared; the first of these yields, with phenol, a compound,

$$OPh{\cdot}PO{\cdot}(NH{\cdot}C_6H_3Cl_2)_2,$$

melting at 227°, and decomposed by boiling water. *Oxyphosphazoparatoluenetoluidide*, $C_6H_4Me{\cdot}N{:}PO{\cdot}NH{\cdot}C_6H_4Me$, 328°; *bromoparatoluidine* [$Me : Br : NH_2 = 1 : 3 : 4$] yields an analogous derivative which is converted by hot acetic acid into the compound

$$(C_6H_3MeBr{\cdot}NH)_3PO,$$

melting at 268°, and by phenol into the compound

$$OPh{\cdot}PO{\cdot}(NH{\cdot}C_6H_3MeBr)_2,$$

melting at 221°. *Oxyphosphazoorthotoluenetoluidide*, 309°. *Oxyphosphazo-compounds* of *mesidine* and *pseudocumidine*,

$$C_6H_2Me_3{\cdot}N{:}PO{\cdot}NH{\cdot}C_6H_2Me_3,$$

were also prepared; they melt at 240° and 217° respectively.

C. F. B.

**Production of Gaseous Formaldehyde.** By ANDRÉ BROCHET (*Compt. rend.*, 1896, **122**, 201—203).—The incomplete combustion of methylic alcohol yields only a small quantity of formaldehyde, accompanied by a large quantity of water and a notable proportion of carbonic oxide. The preparation of the gaseous aldehyde for purposes of disinfection is best accomplished by passing a current of hot gas over coarsely powdered trioxymethylene. The dilution of the aldehyde prevents repolymerisation, and the absence of water vapour makes it possible to apply the method to the disinfection of books, papers, and other articles that would be injured by moisture.

C. H. B.

**Aldehydes derived from the Isomeric Alcohols $C_{10}H_{18}O$.** By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 84—86).—The aldehydes obtained by the oxidation of licareol, licarhodol and geraniol (lemonol) were converted into semicarbazones (this vol., i, 311), and yielded the compounds previously described in approximately the same proportions. It follows that all three aldehydes are mixtures of the same compounds. The aldehyde of licareol was not obtained, because the sulphuric acid converts the licareol into licarhodol, $CH_2{:}CMe{\cdot}C(CH_2{\cdot}OH){\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2$, becoming $CH_2{:}CMe{\cdot}CH(CH_2{\cdot}OH){\cdot}CH_2{\cdot}CH{:}CMe_2$. On the other hand, licarhodaldehyde in presence of sulphuric acid is largely converted into lemonaldehyde, and the change is not reversible;

$$CH_2{:}CMe{\cdot}CH(CHO){\cdot}CH_2{\cdot}CH{:}CMe_2$$

becomes $CMe_2{:}C(CHO){\cdot}CH_2{\cdot}CH{:}CMe_2$.

The aldehyde in oil of lemon consists mainly of lemonaldehyde, with small quantities of licarhodaldehyde. C. H. B.

**Preparation of Glyoxal.** By LEOPOLD SPIEGEL (*Chem. Zeit.*, 1895, **19**. 1423).—In preparing glyoxal by Ljubawin's method (compare Abstr., 1878, 23), much labour may be saved, and the yield of substance increased if the oxidation is at first carried out in a freezing mixture, and the temperature allowed gradually to rise to 25°; if now the acetic acid is distilled off under a pressure of 25—30 mm., the formation of oxalic acid may be entirely avoided, and the brittle, colourless, somewhat gummy, residual mass has all the properties of pure glyoxal. A somewhat better yield is obtained if, before distillation, the oxidation mixture is allowed to remain until all odour of aldehyde has disappeared. A. L.

**Preparation of Acid Fluorides.** By ALBERT COLSON (*Compt. rend.*, 1896, **122**, 243—244).—Acid fluorides can be prepared in the same manner as acid chlorides and bromides (this vol., i, 282). When acetic anhydride is saturated with dry hydrogen fluoride, acetic fluoride is formed, with very great development of heat. It boils at 20·8° under a pressure of 770 mm.; sp. gr. = 1·0369 at 0°. *Propionic fluoride*, obtained in a similar way, boils at 43·5° under a pressure of 765 mm.; sp. gr. = 0·974 at 10°; vapour density normal. It is slowly attacked by water, but rapidly by solutions of alkalis.

Instead of passing hydrogen fluoride into the acid anhydrides, a mixture of the anhydride and sulphuric acid may be allowed to act on sodium hydrofluoride, $NaHF_2$. C. H. B.

**Acid Fluorides.** By MAURICE MESLANS and F. GIRARDET (*Compt. rend.*, 1896, **122**, 239—242).—Acid chlorides act on many metallic fluorides, but the acid fluorides are best obtained by the action of the corresponding chlorides on dry zinc fluoride. The action takes place without extraneous heating, and the yield is almost quantitative.

*Propionic fluoride* is a colourless, very mobile liquid, which boils at 44°; sp. gr. = 0·972 at 15°. *Benzoic fluoride* has a very irritating odour, and boils at 154°. Both fluorides attack glass rapidly in presence of traces of moisture, but are only slightly soluble in, and slowly decomposed by, water. They are, however, rapidly attacked by solutions of alkalis, react slowly with alcohols to form ethers, and rapidly with ammonia, forming amides. C. H. B.

**The Composition of Wool-fat.** By L. DARMSTAEDTER and ISAAC LIFSCHÜTZ (*Ber.*, 1896, **29**, 618—622; compare this vol., i, 198).—The fractions previously obtained by the neutralisation of the alcohols of wool-fat have been further examined, and have been found to consist of the potash salts of myristic acid and carnaubic acid (Stürcke, Abstr., 1884, 1280). These two acids make up about 10—12 per cent. of the whole mass. A. H.

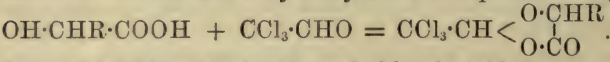
**Cerotic acid and Melissic acid, the Free acids of Beeswax.** By THEOD. MARIE (*J. Pharm.*, 1896, [6], **3**, 107—111; compare Abstr., 1895, i, 81).—Cerotic acid melts at 77·9° (corr.). The crystals deposited from alcohol vary according to the purity of the acid; if it contains neutral substances, it forms a gelatinous mass consisting of microscopic needles, and containing a large proportion of alcohol; if melissic acid is present, short, granular crystals are rapidly deposited. Pure cerotic acid crystallises in stellate, microscopic needles; from benzene, it separates in dense laminæ; from ether, it is deposited in tabular masses consisting of large, aggregated needles. The methylic salt is deposited in pearly needles melting at 62·5°. Nafzger's compound (m. p. 60°) was probably a mixture of methylic cerotate and methylic melissate. Its solubility resembles that of the acid. The ethylic salt is less lustrous, and more readily soluble in ether than the preceding compound, and melts at 60·5°. The *barium salt*, $(C_{25}H_{49}O_2)_2Ba$, is deposited in dense, reticulated crystals. The *magnesium salt* is not deposited when magnesium acetate is added to boiling alcoholic cerotic acid solution (1 per cent.), but, if the liquid is cooled to 50°, a copious precipitate is formed, which does not redissolve on boiling; a mixture of cerotic and melissic acids gives an immediate precipitate with magnesium acetate under these conditions. The *silver salt* is flocculent. Melissic acid resembles cerotic acid in appearance, but crystallises more readily, is almost insoluble in warm methylic alcohol and ether, and melts at 90·6° (corr.). The *methylic* and *ethylic salts* resemble the corresponding cerotates and melt at 74·5° and 73° respectively; the ethylic salt is more readily soluble in ether than the free acid. J. B. T.

**Glycerylic Cerotates and Melissates.** By THEOD. MARIE (*J. Pharm.*, 1896, [6], **3**, 171—177; compare preceding abstract).—Glycerylic cerotates and melissates are readily prepared by heating glycerol with cerotic and melissic acids, but apparently they do not occur naturally. *Glycerylic cerotate*, $C_{24}H_{49}\cdot COO\cdot C_3H_5(OH)_2$, formed by heating the compounds during 10 hours at 178—180°, is readily soluble in alcohol, ether, and benzene, crystallises in laminæ composed of slender needles, and melts at 78·75°. It is also obtained by the action of silver cerotate on chlorhydrin at 180°. The *dicerotate*, prepared by heating glycerol and the acid at 220° during six hours, resembles the preceding compound, but is less soluble, and melts 79·5°. The *tricerotate* crystallises in slender needles, melting at 76·5—77°. Cerotic acid and the monocerotate are formed by heating trichlorhydrin and silver cerotate at 150—160°; below this temperature, the compounds do not interact. *Glycerylic melissate*, $C_{29}H_{59}\cdot COO\cdot C_3H_5(OH)_2$, is prepared in the same manner as the cerotate, which it closely resembles, and melts at 91·5—92°. The *dimelissate* and *trimelissate* resemble the corresponding cerotates, and melt at 93° and 89° respectively.

J. B. T.

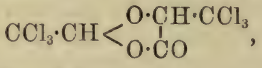
**Alloisomerism, a Rejoinder to Michael.** By CARL T. LIEBERMANN (*J. pr. Chem.*, 1896, [2], **53**, 255—256).—Michael's laws of alloisomerism (this vol., i, 133) cannot be brought into accord with some of the author's experimental results; it is the laws that are at fault. A. G. B.

**Action of Chloral on Hydroxy-acids in Presence of Sulphuric acid.** By LAZAR EDELEANU and AL. ZAHARIA (*Chem. Centr.*, 1895, ii, 212—213; from *Bul. Soc. Sci. fizice Bucur Romănia*, **4**, 13—15). —Wallach has shown that in presence of sulphuric acid the interaction of chloral and $\alpha$-hydroxy-acids is represented by the equation,



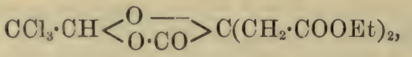
$$OH{\cdot}CHR{\cdot}COOH + CCl_3{\cdot}CHO = CCl_3{\cdot}CH{<}\begin{matrix}O{\cdot}CHR\\ |\\ O{\cdot}CO\end{matrix}.$$

Ethylic $\alpha$-hydroxy-$\beta$-trichloropropionate and chloral yield the compound,



$$CCl_3{\cdot}CH{<}\begin{matrix}O{\cdot}CH{\cdot}CCl_3\\ |\\ O{\cdot}CO\end{matrix},$$

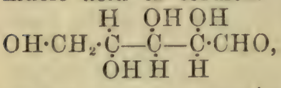
which melts at 114—115°. Ethylic hydrogen sulphate is also formed. Ethylic citrate under similar conditions gives the compound,



$$CCl_3{\cdot}CH{<}\begin{matrix}O\text{———}\\ O{\cdot}CO\end{matrix}{>}C(CH_2{\cdot}COOEt)_2,$$

which melts at 73°. The *methylic* derivative is oily, and readily reacts with phenylhydrazine. J. B. T.

**A New Pentonic acid and Pentose.** By EMIL FISCHER and OTTO BROMBERG (*Ber.*, 1896, **29**, 581—585).—Xylonic acid prepared by oxidising xylose with bromine, and isolated by means of the double salt which its cadmium salt forms with cadmium bromide, was heated with pyridine for 3½ hours at 135°. Unchanged xylonic acid was then removed as the cadmium double salt, and from the residue the *lactone*, $C_5H_8O_5$, of a new pentonic acid, *lyxonic acid*, was obtained by extraction with ethylic acetate. The lactone melts at 113—114° (corr. 114—115°), and has a specific rotation $[\alpha]_D = +82{\cdot}4°$ at 20°; it is partly converted back again into xylonic acid when it is heated with pyridine. The *brucine salt* of the acid melts at 174—176° (corr.); the *phenylhydrazide* at 164—165° (corr.). The lactone can be reduced with 2½ per cent. sodium amalgam at 0° to the sugar, *lyxose*, which was obtained as an impure lævorotatory syrup. When its cyanhydrin is prepared and hydrolysed with baryta, and the product oxidised with nitric acid, mucic acid is formed. The structure of the sugar is probably



$$OH{\cdot}CH_2{\cdot}\overset{H}{\underset{OH}{C}}{-}\overset{OH}{\underset{H}{C}}{-}\overset{OH}{\underset{H}{C}}{\cdot}CHO,$$

in which case its systematic name is *pentose* — — +, or *pentanetetronal* — — +. C. F. B.

**Action of Inorganic acids of the Metals on Organic acids.** By ARTHUR ROSENHEIM (*Zeit. anorg. Chem.*, 1896, **11**, 225—248).—In order to obtain further information with reference to the constitution of the complex acids derivable from oxalic acid and the acidic oxides of molybdenum, tungsten, vanadium, aluminium, chromium, and iron, the author has determined the conductivities and ionic migration constants of some of these compounds and their salts. The results generally confirm the views put forward in his previous paper (this vol., i, 278). It appears that in these compounds the original avidity of the oxalic acid is much reduced, and that their formation depends on the relative affinities of their components, the one evidently acting as a base towards the other, both together then, in virtue of their acid properties, possessing a residual affinity for strong bases. H. C.

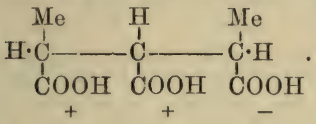
**Stereoisomeric Dimethyltricarballylic acids.** By Nicolai D. Zelinsky (*Ber.*, 1896, **29**, 616—618; compare this vol., i, 281).—The electric conductivities of the three inactive dimethyltricarballylic acids previously described by the author fit into the series of substituted tricarballylic acids, the numbers being as follows.

| | M. p. | |
|---|---|---|
| Tricarballylic acid ........ | — | 0·022 |
| Methyltricarballylic acid... | — | 0·032 |
| Dimethyltricarballylic acid. | 148—149° | 0·051 |
| | 175—176 | 0·054 |
| | 203—204 | 0·042 |

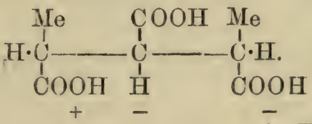
If one of the acids were a methylcarboxyadipic acid,

$$\mathrm{COOH{\cdot}CHMe{\cdot}CH(COOH){\cdot}CH_2{\cdot}CH_2{\cdot}COOH},$$

it is probable that the conductivity would be less than is required for this series; the author therefore believes that the three substances are stereoisomeric, and supposes that in addition to the racemic form of the fumaroïd acid, two inactive malenoïd forms may exist.



$$\begin{array}{ccccc} \mathrm{Me} & & \mathrm{H} & & \mathrm{Me} \\ \mid & & \mid & & \mid \\ \mathrm{H{\cdot}C} & \text{——} & \mathrm{C} & \text{——} & \mathrm{C{\cdot}H} \\ \mid & & \mid & & \mid \\ \mathrm{COOH} & & \mathrm{COOH} & & \mathrm{COOH} \\ + & & + & & - \end{array} .$$



$$\begin{array}{ccccc} \mathrm{Me} & & \mathrm{COOH} & & \mathrm{Me} \\ \mid & & \mid & & \mid \\ \mathrm{H{\cdot}C} & \text{——} & \mathrm{C} & \text{——} & \mathrm{C{\cdot}H.} \\ \mid & & \mid & & \mid \\ \mathrm{COOH} & & \mathrm{H} & & \mathrm{COOH} \\ + & & - & & - \end{array}$$

A. H.

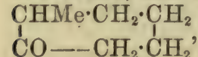
**A Contribution to Nomenclature.** By M. M. Richter (*Ber.*, 1896, **29**, 586—608).—The author publishes proposals for a uniform system of chemical nomenclature for ring compounds and their derivatives, largely supplementary to the proposals of the Geneva Congress (1892). He does this in deference to the wishes of Beilstein and others, who desire that his system should be publicly discussed, in order that by this means the way may be prepared for the introduction at a future congress of a consistent and satisfactory system of nomenclature. It is impossible to give a satisfactory abstract of the paper; those interested must consult the original. It may be said, however, that trivial names are entirely discarded in the case of compounds of known structure, and strictly systematic names are introduced instead; benzene, for example, is "⑥ hexene," and pyrroline is "⑤ penteneazene (1)." Ring compounds are chiefly dealt with, the Geneva Congress having already considered open chain compounds in some detail. Rings of 3, 4, 5, 6, 7, ...... members are denoted propene, butene, pentene, hexene, heptene, ....... These names are themselves used if all the members of the ring are CH groups; other elements or groups present are indicated by the addition of the following affixes, which are to be used in the order given if groups of more than one kind are present. O, oxene; S, sulphene; Se, selene; NH, azene; PH, phosphene; $SO_2$, sulphonene; N, azine; P, phosphine; As, arsine; $I'''$, iodine; $I^v$, iodonium; $N^v$, azonium. The numbering of the rings is very carefully carried out, each member, without exception, receiving a number. The position of groups in the ring itself is indicated by a number placed in brackets, whereas a number without brackets is used to indicate the position of a substituting group of the ordinary kind; in each case the number *follows* the name of the group to which it applies. α-Methylpyridine, for example, would be "⑥ hexeneazine (1)-methyl-2." In the case of mixed open and closed chain compounds, an elaborate scheme is developed, by means of which it is possible to indicate without ambiguity the position of any substituting group; when it is necessary to distinguish positions in a ring from those in an open chain, the numbers referring to the ring have a ° placed over them; thus, $C_6H_5\cdot CH_2\cdot CH_2Cl$ would be "⑥ hexene-ethyl-$\overset{\circ}{1}$-chlor-$\overset{\circ}{1}^2$," meaning that the chlorine atom is attached to the second carbon atom of an ethyl chain that is joined to the carbon atom 1 of the ring. If two or more chains branch from one carbon atom, positions in the largest are denoted by a simple index, for example, $^2$; those in the next and in the smallest respectively by a singly and doubly underlined index, for example $^{\underline{2}}$ and $^{\underline{\underline{2}}}$. This system makes it possible to name at once any compound the existence of which can be foreseen as possible.

The great advantage of the system would be that ring compounds could be named readily, and without ambiguity. The names are, however, sometimes too cumbrous even for the purpose of indexing; it is proposed that for this purpose compounds should be first classified according to their aggregate molecular formulæ, as is done in the author's *Tabellen der Kohlenstoffverbindungen;* under every such formula would be arranged the various compounds to which it corresponds. C. F. B.

**The Hexamethylene Series. IV. Synthesis of Heptanaphthene.** By NICOLAI D. ZELINSKY and A. GENEROSOFF (*Ber.*, 1896, **29**, 729—733).—*α-Methylpimelic acid*,

$$COOH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH,$$

is prepared from ethylic α-cyanopropionate by the action of trimethylenic bromide and alcoholic sodium ethoxide and then treating the product, which boils at 160—163° (13 mm. pressure), with ethylic sodiomalonate. The *ethylic* salt, $C_{16}H_{25}NO_6$, thus obtained boils above 170° (75 mm. pressure), and yields the methylpimelic acid when boiled with sulphuric acid. The acid boils at 223—224° (15 mm. pressure), and melts at 57—58°. It has a conductivity ($K$) of 0·00315, and is tribasic to baryta water. *Methylketohexamethylene*,



$\begin{array}{l}CHMe\cdot CH_2\cdot CH_2\\ | \qquad\qquad\quad |\\ CO—CH_2\cdot CH_2\end{array}$, is obtained by distilling the acid with quicklime. It is a colourless liquid with a pleasant odour, boils at 165—166°, and has the sp. gr. = 0·9246 at 18°/4°. It readily yields an additive compound with sodium hydrogen sulphite. When reduced, it is converted into the *alcohol*, which boils at 168—169°, and has a sp. gr. 0·9225 at 17°/4°. Methylhexamethylene (heptanaphthene), $C_7H_{14}$, is formed when the alcohol is reduced with hydriodic acid at 230°. It boils at 101—102°, has the molecular refraction 32·36, and behaves in every way as a saturated hydrocarbon. It appears to be identical with the heptanaphthene isolated by Milkowsky (*Journ. Rus. Chem.*, **17**, [2], 38; **15**, 554), and the hexahydrotoluene of Markownikoff (*J. pr. Chem.*, 1894, 431). When treated with aluminium bromide and bromine, it yields pentabromotoluene. A. H.

**Acids obtained in refining Petroleum.** By FUCHS and SCHIFF (*Chem. Zeit.*, 1895, **19**, 1469).—In the hope of turning to account the fruit-like odours of ethereal naphthenecarboxylates, the authors have investigated the alkaline residues obtained from an Austrian refinery. The oils obtained were readily saponified by soda-lye, yielding a soap with a disagreeable odour of fatty acids. The acids, obtained on decomposing the soap, consisted of an octonaphthenecarboxylic and a nononaphthenecarboxylic acid, the latter preponderating. The mixed acids were converted into their ethylic salts, and separated into two fractions boiling at 215—225° and 225—235° respectively. The ethylic salts had, in the concentrated state, a pleasant fruity odour, which, however, in a diluted condition, was completely altered in character, becoming unpleasantly reminiscent of snuff. The authors suggest the use of this property as a ready means of discrimination between fatty and naphthenecarboxylic acids. A. L.

**Hydrogenation of Normal Propylbenzene. Pentabromopropylbenzene.** By A. E. TCHITCHIBABIN (*J. Russ. Chem. Soc.*, 1894, **26**, 40—45).—The propylbenzene employed for the experiments was prepared by Fittig's method, and its hydrogenation effected by heating it for 24 hours at 270—280° with hydriodic acid of sp. gr. over 2. The most suitable proportion is about 0·6 c.c. of the substance and 20 c.c. of the acid; the product, which distilled completely at about 148°, was purified by treatment in the cold with fuming nitric acid, and after washing and drying, subjected to repeated fractional distillation. The main fraction, boiling at 140—142°, formed about half of the whole product, and on analysis and a determination of the vapour density, was found to have the formula $C_9H_{18}$. Its sp. gr. = 0·7819 at 0°/0°.

The action of bromine on propylbenzene in the presence of aluminium bromide, gives rise to pentabromopropylbenzene. The presumption that, under the same conditions the hydrocarbon, $C_9H_{18}$, would give a pentabromo-derivative was not verified, a crystalline substance being obtained, melting at 230°, and soluble in ether or benzene, less so in hot, and almost insoluble in cold alcohol. A bromine determination indicated the formula $C_9H_9Br_3$, and from its melting point, appearance, and solubility it would appear to be identical with tribromopseudocumene. If this be so, the presence of hexahydropseudocumene in the hydrocarbon, $C_9H_{18}$, can only be explained by the action of iodine, set free during the process of hydrogenation.

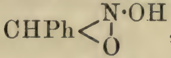
An analogous case has been noticed by Raýman and Preiss (Abstr., 1884, 1311), who obtained a series of aromatic hydrocarbons by the action of iodine on cymene. On the other hand, although the specific gravity of hexahydropseudocumene, namely, 0·7812, is very near that of the product obtained by hydrogenation, the difference in the boiling points (hexhydropseudocumene 135—138°, the other compound 142°) is too considerable for them to be identical. S. G. R.

**The Benzene Nucleus.** By Wilhelm Vaubel (*J. pr. Chem.*, 1896, [2], **53**, 241—245; compare Abstr., 1894, i, 325, 501; 1895, i, 53, 339; this vol., i, 213).—The author explains, by the light of his configuration for benzene, certain cases in which meta-derivatives are formed when ortho- and para- may be reasonably expected, certain extraordinary changes on the part of meta-derivatives, and the changes incident to the complete chlorination of benzene and its homologues. A. G. B.

**Nitration of Bromobenzene.** By John H. Coste and Ernest J. Parry (*Ber.*, 1896, **29**, 788—792).—The authors have investigated the preparation of bromonitrobenzenes under varying conditions. The para-compound readily dissolves when boiled with dilute methylated spirit (1 : 1); but at the ordinary temperature its solubility is only 0·1 gram in 100 c.c.; the ortho-compound is much more readily soluble, and is gradually deposited from the mother liquor; after treatment in this manner, the fractions show the correct melting point. (1) Fuming (red) nitric acid (20 c.c.) is heated on the water bath, and bromobenzene (10 c.c.) gradually added below the surface of the acid. The total yield is 66·3 per cent. of the theoretical; para : ortho = 1 : 0·53. (2) Conditions as before, but the experiment conducted at the ordinary temperature. The total yield is 95·2 per cent. of the theoretical; para : ortho = 1 : 0·65. The poor yield in the first experiment was due to the readiness with which both compounds volatilise either when heated alone at 100°, with steam, or with acid vapours. (3) Nitric acid (sp. gr. = 1·42, 15 c.c.) is mixed with concentrated sulphuric (15 c.c.) and bromobenzene (10 c.c.) added to the well-cooled liquid; when the action slackens, it is completed by gently warming. The total yield is 97·7 per cent. of the theoretical; para : ortho = 1 : 0·44. (4) Bromobenzene (20 c.c.) is mixed with glacial acetic acid (20 c.c.) and nitric acid (20 c.c.), and heated until the liquid becomes clear, concentrated sulphuric acid (20 c.c.) is then added, nitrous anhydride is copiously evolved, and the action is completed in about five minutes. The yield is 89·4 per cent. of the theoretical; para : ortho = 1 : 0·51. Attempts to prepare the nitrobromobenzenes from the nitracetanilides were unsatisfactory; the yield was poor, and the products difficult to purify. Bromobenzene, when heated for some time with ordinary concentrated nitric acid, yields only traces of nitro-derivatives. J. B. T.

**Derivatives of Unsymmetrical Tribromobenzene.** By C. Loring Jackson and F. B. Gallivan (*Amer. Chem. J.*, 1896, **18**, 238—252).—The main facts have already appeared (Abstr., 1895, i, 212). *Tribromaniline sulphate*, $C_6H_2Br_3\cdot NH_3SO_4H$ [$Br_3 : NH_3SO_4H = 2 : 4 : 5 : 1$], crystallises from water in white plates, and from alcohol in needles. The corresponding *chloride* and *bromide* crystallise from alcohol in white, branching needles. 2 : 4 : 5-*Tribromacetanilide* melts at 188°, and crystallises from alcohol in microscopic, radiating needles. J. F. T.

**Isomeric Phenylnitromethanes.** By ARTHUR R. HANTZSCH and OTTO W. SCHULTZE (*Ber.*, 1896, **29**, 699—703).—Phenylnitromethane (exonitrotoluene) is best prepared by adding silver nitrite to an ethereal solution of benzylic iodide at 0°; the yield is 30 per cent. of the theoretical. From its sodium salt, it is set free by acetic acid or carbonic anhydride in the form of an oil, as is well known; mineral acids liberate, at not too high a temperature, white crystals which melt at 74—76°. These represent an isomeric form of the oily substance; they are transformed into the latter when heated to the boiling point in ethereal or alcoholic solution, or if allowed to remain at the ordinary temperature in contact with hydrochloric acid, or in solution in benzene. The crystalline differs from the oily isomeride in that it gives a reddish-brown coloration with ferric chloride, and it also dissolves much more readily in aqueous alkali carbonates, no carbonic anhydride being evolved, however. It is suggested that the new isomeride has the constitution



$\mathrm{CHPh}<\begin{matrix}\mathrm{N\cdot OH}\\ | \\ \mathrm{O}\end{matrix}$

, and that, when an ordinary nitro-paraffin forms a sodium salt, it undergoes a molecular transformation into an isomeride with a structure similar to this. The new substance is certainly not identical with benzhydroxamic acid, $OH\cdot CPh\colon NOH$. C. F. B.

**Combination of Aluminium Chloride with Phenols and their Derivatives.** By G. PERRIER (*Compt. rend.*, 1896, **122**, 195—198).—Ketones, nitriles, ethers, &c., combine with aluminium chloride in the proportion of 2 mols. of the former to 1 mol. of the latter, without any elimination of hydrogen chloride, the products being additive compounds. Phenols behave differently, for whilst the molecular proportions remain the same, 2 mols. of hydrogen chloride are eliminated, and substitution products of the composition $Al_2Cl_4(OR')_2$ are formed. In presence of water, the original phenol is regenerated, and basic aluminium chloride, $Al_2Cl_4(OH)_2$, is formed. All the compounds are solid, and some of them crystallise readily; they are insoluble in carbon tetrachloride and light petroleum, but the solubility in carbon bisulphide or alcohol varies with the nature of the phenol. The aluminium chloride and the phenol are mixed directly or in presence of carbon bisulphide, and the mixture is heated towards the close of the reaction.

The products have the following characteristics: *Phenol*, white crystals, which melt at 181—183°, and decompose at about 200°, very soluble in carbon bisulphide and alcohol; *orthonitrophenol*, red needles, which melt at 160—165°, slightly soluble in alcohol and carbon bisulphide; *paranitrophenol*, a yellow powder which melts at 99—100°, and decomposes at about 105°, insoluble in carbon bisulphide, but soluble in alcohol; *orthochlorophenol*, a white, crystalline powder, which melts at 207—210°, and is soluble in alcohol, but only slightly soluble in carbon bisulphide; *parachlorophenol*, colourless crystals, melting at 185—187°, soluble in alcohol and somewhat soluble in carbon bisulphide; *thymol*, colourless crystals melting at 142—145°, and decomposing at 150°, very soluble in carbon bisulphide and in alcohol; *α-naphthol*, small, red crystals, almost insoluble in carbon bisulphide; *β-naphthol*, a yellow powder, likewise insoluble in the bisulphide; *salicylaldehyde* and *methylic* and *phenylic salicylates* yield yellowish products insoluble in carbon bisulphide. C. H. B.

**Water of Crystallisation of Barium Picrate.** By HUBERT G. SHAW (*Amer. Chem. J.*, 1896, **18**, 266—268).—A specimen of barium picrate examined by the author contained $6H_2O$. The amount has been variously stated as $4H_2O$, $5H_2O$, and $6H_2O$. Experiments will be made to ascertain if more than one hydrate exists. J. F. T.

**Action of Sodium Ethoxide on Anethoïl and Monobromanethoïl Dibromides.** By CARL HELL and A. HOLLENBERG (*Ber.*, 1896, **29**, 682—690; compare Wallach and Pond, this vol., i, 94).—When monobromanethoïl dibromide, $OMe{\cdot}C_6H_3Br{\cdot}CHBr{\cdot}CHMeBr$, is boiled with alcoholic sodium ethoxide, an oily compound,

$$OMe{\cdot}C_6H_3Br{\cdot}C(OEt){:}CHMe,$$

boiling at 180—182° under 16 mm. pressure, is obtained. When this compound is treated with acids or with water, or even when it is allowed to remain in contact with air, it becomes hydrolysed, losing alcohol and forming the crystalline ketone $OMe{\cdot}C_6H_3Br{\cdot}CO{\cdot}CH_2Me$; the same substance is formed when it is heated at 270—295° under atmospheric pressure, under which circumstances ethylene is evolved. When treated with bromine (1 mol.), both these compounds yield a ketone, $OMe{\cdot}C_6H_3Br{\cdot}CO{\cdot}CHMeBr$, melting at 99°, or with 2 mols. of bromine a ketone, $OMe{\cdot}C_6H_3Br{\cdot}CO{\cdot}CMeBr_2$, melting at 103·5°.

Anethoïl itself yields a similar series of compounds. The compound $OMe{\cdot}C_6H_4{\cdot}C(OEt){:}CHMe$, is an oil boiling at 135—138° under 13 mm., and at 258—260° under atmospheric pressure.

The action of the sodium ethoxide, no doubt, takes place in two stages, as in the case of ethylisoeugenol (this vol., i, 357). In the case of anethoïl, the intermediate product,

$$OMe{\cdot}C_6H_4{\cdot}CH(OEt){\cdot}CHMeBr,$$

has been isolated, and forms an oil which boils at 165—170° under 14 mm. pressure, and loses both alcohol and ethylic bromide when heated at 220°. The corresponding bromanethoïl compound is decomposed in the same way when distilled under diminished pressure, and has not yet been obtained pure. C. F. B.

**Certain Bromine Derivatives of Resorcinol.** By C. LORING JACKSON and F. L. DUNLAP (*Amer. Chem. J.*, 1896, **18**, 117—132).—It has been observed (*Amer. Chem. J.*, **15**, 641) that the diethyl ether of tribromonitroresorcinol, $NO_2{\cdot}C_6Br_3(OEt)_2$, when heated with sodium ethoxide, exchanges 2 atoms of bromine for hydrogen, giving $NO_2 \cdot C_6H_2Br(OEt)_2$. The diethyl ether of tribromoresorcinol, however, does not give up bromine to sodic ethoxide at the boiling point of alcohol, and the dibrom-ether is not attacked below 200°, and is, therefore, more stable than 1 : 3 : 5-tribromobenzene, which is slowly converted into dibromanisoïl at 120—130° (Blau, Abstr., 1887, 242). From tribromoresorcinol, bromine could be removed with great ease, even water at 100° decomposing it. Ethoxyl groups, therefore, do not weaken the attachment of the bromine atoms to the benzene ring, whereas hydroxy-groups exert this loosening action to the same extent as the nitro-groups in tribromodinitrobenzene.

The brown amorphous substances produced by removing bromine from tribromoresorcinol could not be analysed, but appear to be substituted resorcinol ethers, formed by a reaction involving the hydroxyl groups. Ethylic sodiomalonate gave a similar unmanageable product with tribromoresorcinol, but, in addition to this, ethylic ethanetetracarboxylate was isolated.

Tribromoresorcinol diethyl ether is converted by nitric acid into the 2 : 4 : 6 : 5-tribromonitroresorcinol diethyl ether, melting at 101°. The action of nitric acid on dibromoresorcinol diethyl ether was quite different, giving a new *dinitroresorcinol diethyl ether*, melting at 126°, two nitro-groups displacing two bromine atoms. A similar replacement occurred when the tribromoresorcinol was treated with fuming nitric acid, the product being the bromodinitroresorcinol described by Typke (Abstr., 1883, 915) and Fèvre (*ibid.*, 733).

It is thus proved that hydroxyl and ethoxyl have the same effect on bromine that they have on hydrogen attached to the benzene ring; for just as phenols are much more susceptible to the replacement of their hydrogen by halogens, or nitro-groups than the corresponding hydrocarbons, so the bromine can be replaced by other radicles, including the nitro-group, much more easily in tribromoresorcinol than in tribromobenzene; whilst, on the other hand, the phenol ethers hold their hydrogen or bromine as firmly as the corresponding hydrocarbons. The only exception is the replacement of bromine by $NO_2$, when nitric acid acts on dibromoresorcinol diethyl ether. Towards other reagents, however, such as sodium ethoxide, the dibromo-ether shows the same stability as the tribromo-ether.

The debromination of tribromoresorcinol diacetate was attempted, but it was converted into tribromoresorcinol by the reagents used, and consequently the products were the same as those above mentioned. With fuming nitric acid, the diacetate gives *tribromonitroresorcinol diacetate*, which crystallises in yellowish-white prisms, and melts at 161°. The *sodium derivative* of tribromoresorcinol was obtained in short, flat, white prisms by precipitating an ethereal solution with alcoholic sodium ethoxide, and apparently contained 2 mols. of alcohol of crystallisation. After standing for a short time, even in a vacuum or in hydrogen, it suddenly turned black, evolving alcohol vapour and developing heat; the black residue gave up to water sodium bromide and a black salt, but neither this nor the red, amorphous substance left undissolved could be analysed.

*Dibromoresorcinol diethyl ether*, $C_6H_2Br_2(OEt)_2$, prepared by adding bromine to a solution of resorcinol diethyl ether in glacial acetic acid, crystallises in long, slender, white, silky prisms, and melts at 99—100°. *Tribromoresorcinol diethyl ether*, prepared from the foregoing with excess of bromine, crystallises in long, pearly fibres, and melts at 68—69°. Tribromoresorcinol, prepared by Benedikt's method (*Monatsh.*, **4**, 227), was found, after recrystallisation from water, to have the melting point given by him, whereas Typke (*Ber.*, **10**, 1578) gives 104°. Hlasiwetz and Barth state that it crystallises with $2H_2O$, but it was found to be anhydrous. Tribromoresorcinol is gradually decomposed by boiling water, bromine being removed, and a dark red, amorphous substance formed. Aniline and sodium ethoxide also remove bromine, but in none of these cases could any organic product be isolated in a state fit for analysis. A. E.

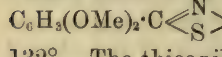
**Derivatives of Veratrol.** By FR. BRÜGGEMANN (*J. pr. Chem.*, 1896, [2], **53**, 250—254).—*Tetrachloroveratrol*, $C_6Cl_4(OMe)_2$, prepared by chlorinating veratrol in carbon tetrachloride, crystallises from alcohol in white needles, and melts at 88°; when heated with excess of strong sulphuric acid, it is converted into *tetrachloroguaiacol*, $(OH)C_6Cl_4(OMe)$, which melts at 185—186°.

*Tetrabromoveratrol* is prepared by the action of excess of bromine on a solution of veratrol in strong sulphuric acid; it crystallises from ether in white needles, and melts at 118°. Strong sulphuric acid does not convert it into a guaiacol.

*Diiodoveratrol*, $C_6H_2I_2(OMe)_2$, prepared by the action of iodine and mercuric oxide on an alcoholic solution of veratrol, crystallises in white needles, and melts at 125°.

By nitrating a sulphuric acid solution of veratrol, a *dinitroveratrol*, $C_6H_2(NO_2)_2(OMe)_2$, is obtained, which crystallises in yellowish-brown needles, and melts at 127—128°. By heating nitroveratrol with strong nitric acid in a sealed tube, a second dinitroveratrol, crystallising in yellow needles and melting at 127°, is obtained; this is probably identical with Merck's dinitroveratrol. The isomerism of the two dinitroveratrols is confirmed by the fact that 100 c.c. of alcohol at 15° dissolve 0·3892 gram of the compound melting at 127—128°, and 0·2660 of that melting at 127°.

*Benzoylveratrol*, $C_6H_3Bz(OMe)_2$, is formed by the action of benzoic chloride on veratrol in presence of aluminium chloride; it crystallises in aggregates of white needles, and melts at 99°; the *phenylhydrazone* of this compound melts at 174°. An acetyl analogue could not be prepared. *Benzoylguaiacol*, $OMe{\cdot}C_6H_4{\cdot}OBz$, melts at 57°.

*Veratrol thioanilide*, $C_6H_3(OMe)_2{\cdot}CS{\cdot}NHPh$, obtained by the action of phenylthiocarbimide on veratrol, in presence of aluminium chloride, crystallises in slender, felted, yellow needles, and melts at 159°. Oxidation with potassium ferricyanide converts it into the *compound*  $C_6H_3(OMe)_2{\cdot}C{<}^{N}_{S}{>}C_6H_4$, which crystallises in needles melting at 132°. The thioanilide is desulphurised by iodine in alcohol, yielding the *veratranilide*; this crystallises in white, felted needles, and melts at 154°. A. G. B.

**Pyrogallol.** By R. Godeffroy (*Chem. Centr.*, 1895, ii, 159; from *Zeit. Österr. Apoth. Verein*, **33**, 377—380; *Pharm. Zeit.*, **40**, 390).—The compound $OH\cdot C_6H_3O_2Ba + 4H_2O$ is deposited in colourless needles, when aqueous pyrogallol is mixed with baryta water in excess; it rapidly blackens when exposed to air, and decomposes when boiled with water. Alcoholic pyrogallol yields a similar compound with $3H_2O$. J. B. T.

**Action of Sodium Ethoxide on Ethylisoeugenol Dibromide.** By Carl Hell and B. Portmann (*Ber.*, 1896, **29**, 676—682; compare Abstr., 1895, i, 657, and Wallach and Pond, this vol., i, 95).—If sodium ethoxide (1 mol.) in alcoholic solution is allowed to act on ethylisoeugenol dibromide (1 mol.), a compound

$$OMe\cdot C_6H_3(OEt)\cdot CH(OEt)\cdot CHMeBr,$$

is obtained as an oil. If this is heated at 225—230°, or if it is distilled under 15 mm. pressure, when it appears to boil at 185—187°, it loses alcohol, and the compound $OMe\cdot C_6H_3(OEt)\cdot CH{:}CMeBr$, melting at 72°, is formed. This compound takes up 2 atoms of bromine, the product melting at 107°; it does not readily exchange its bromine atom for other groups, but it reacts with sodium ethoxide, and the product is a compound, $OMe\cdot C_6H_3(OEt)\cdot C{:}CMe$, which, curiously, only takes up 2 atoms of bromine.

In the light of these facts it is necessary to regard the action of excess of sodium ethoxide on an aromatic propenyl dibromide, with subsequent hydrolysis of the product, as taking place in the following stages: $R\cdot CHBr\cdot CHMeBr \rightarrow R\cdot CH(OEt)\cdot CHMeBr \rightarrow$

$$R\cdot C(OEt){:}CHMe \rightarrow R\cdot C(OH){:}CHMe \rightarrow R\cdot CO\cdot CH_2Me.$$

Sodium reduces the compound $OMe\cdot C_6H_3(OEt)\cdot CH{:}CMeBr$ to dihydroethyleugenol, $OMe\cdot C_6H_3(OEt)\cdot CH_2\cdot CH_2Me$, and when potassium acetate acts on ethylisoeugenol dibromide, only one bromine atom is displaced, and a compound, $OMe\cdot C_6H_3(OEt)\cdot CH(OAc)\cdot CHMeBr$, is formed, which loses acetic acid when distilled, and forms the compound $OMe\cdot C_6H_3(OEt)\cdot CH{:}CMeBr$. C. F. B.

**Structure of the Product of Oxidation of Paratoluidine.** By Jacob N. Barsilowsky (*J. Russ. Chem. Soc.*, 1894, **26**, 52—55).—Reference is made to a paper by Green (Trans., 1893, 1395) on the structure of a compound which was originally obtained by the author in 1873, although he has not published his results until now. It was formed, together with parazotoluene, by the oxidation of paratoluidine, and had the same elementary composition as azotoluene, namely, $C_7H_7N$. The author obtained the same compound by the oxidation of paratolylparatolylenediamine, $NH_2\cdot C_6H_3Me\cdot NH\cdot C_7H_7$ [1 : 4 : 3]. The mean of several determinations of the molecular weight by Raoult's method, using benzene as solvent, is 310, which agrees with the formula, $(C_7H_7N)_3 = 315$, and is also in accordance with the figure found by Green, namely 320.

On heating the hydrochloride of the compound, the hydrochloride of another base is formed, which could not be obtained in a state of purity, as it rapidly oxidises, forming a dark brown oxy-base, to which the author, as well as Klinger and Pitschke (Abstr., 1885, 151), have assigned the name of *rosotoluidine*. Its molecular weight was found to be 220, corresponding with the formula $C_{14}H_{14}N_2O = 226$.

S. G. R.

**Condensation of Aldehydes with Aromatic Amines.** By Jacob N. Barsilowsky (*J. Russ. Chem. Soc.*, 1894, **26**, 51—52).—The results of the author's investigation on the condensation of benzaldehyde, and of the three isomeric nitrobenzaldehydes, with azobenzene (*J. Russ. Chem. Soc.*, 1893, **23**, 47), have led him to conclude that the usual explanation of the action which takes place during the condensation of the above-named aldehydes with the salts of aromatic amines in the presence of zinc chloride is not justified. From a long series of experiments on the condensation, under varied conditions, of these aldehydes with free aniline and its salts in the presence of zinc chloride, it appears that in the first phase of the reaction benzylideneaniline, $CHPh{:}NPh$, boiling at 51·5°, and also three isomeric nitrobenzylideneanilines, ortho-, meta-, and para-, boiling respectively at 89·5°, 64—65°, and 65—66° are formed, which then react with the salts of aniline, giving derivatives of triphenylmethane, namely, diamidotriphenylmethane and three isomeric nitrodiamidotriphenylmethanes. S. G. R.

**Action of Phenylhydrazine on Nitrosophenols.** By Giuseppe Plancher (*Gazzetta*, 1895, **25**, ii, 379—394).—On treating nitrosophenol suspended in benzene with phenylhydrazine, a good yield of paramidophenol is obtained; no azoxyphenol could be extracted from the resinous residue, as was done by Fischer and Wacker (Abstr., 1888, 1286), operating in ethereal solutions.

Paramidothymol is obtained by the action of phenylhydrazine on nitrosothymol in benzene solution; it melts at 177·5—179°, not at 176—177°, as stated by Liebermann and Ilinski (*Ber.*, **18**, 3199). Its *hydrochloride*, $OH\cdot C_{10}H_{12}\cdot NH_2,HCl$, is a white, crystalline substance, melting at 255°; it gradually evolves hydrogen chloride and turns blue. *Acetamidothymol*, $OH\cdot C_{10}H_{12}\cdot NHAc$, prepared by the aid of acetic anhydride, forms small, white needles, which redden on exposure, and melt at 174—175°. *Diacetamidothymol*, $OH\cdot C_{10}H_{12}\cdot NAc_2$, obtained by the further action of acetic anhydride, crystallises in colourless scales melting at 88—90°. *Benzamidothymol*,

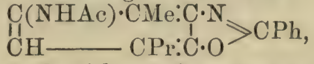
$$OH\cdot C_{10}H_{12}\cdot NHBz,$$

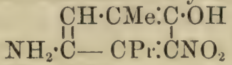
crystallises in colourless needles melting at 178—179°; *benzamidobenzoylthymol*, $OBz\cdot C_{10}H_{12}\cdot NHBz$, crystallises in white needles melting at 166—167°. *Benzylideneamidothymol*, $OH\cdot C_{10}H_{12}\cdot N{:}CHPh$, obtained by heating paramidothymol with benzaldehyde at 120—125°, crystallises in yellowish prisms melting at 148—150°; it yields *benzylideneamidoacetylthymol* (?) when treated with acetic anhydride. Paramidothymol and metabenzaldehyde yield a yellow *substance* melting at 161—162°. *Cumylideneparamidothymol*, $OH\cdot C_{10}H_{12}\cdot N{:}CH\cdot C_6H_4Pr$, melts at 153—154°.

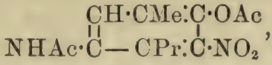
A good yield of paramidocarvacrol is obtained by the action of phenylhydrazine on nitrosocarvacrol in benzene solution; its *hydrochloride* melts at 280° with slight previous decomposition, and its *acetyl* derivative, $OH\cdot C_{10}H_{12}\cdot NHAc$, forms large, colourless crystals, melting at 176—177°.

1-Nitroso-β-naphthol and hydrazine react in benzene or alcoholic solution, yielding the amido-β-naphthol of Stenhouse and Groves (*Annalen*, **189**, 153). 4-Nitroso-α-naphthol similarly yields Liebermann and Dittler's amidonaphthol, whilst the 2-nitroso-α-naphthol, melting at 152°, gives 2-amido-α-naphthol. W. J. P.

**Dinitramidothymol and Dinitramidocarvacrol.** By MARIANO SODERI (*Gazzetta*, 1895, **25**, ii, 401—407).—On reducing dinitrothymyl benzoate (Mazzara, Abstr., 1891, 46) with tin and hydrochloric acid, amidobenzamidothymol and *nitramidothymylic benzoate*, $NO_2\cdot C_6HMePr(NH_2)\cdot OBz$, are obtained; the latter crystallises in yellow needles melting at 158—160°, and, on treatment with alcoholic potash, yields *nitramidothymol*, $NO_2\cdot C_6HMePr(NH_2)\cdot OH$, which crystallises in long, reddish needles. With acetic anhydride, it gives *acetamidonitrothymylic acetate*, $NO_2\cdot C_6HMePr(NHAc)\cdot OAc$, which crystallises in small, yellow prisms melting at 157—159°.

*Acetamidobenzamidothymol*,  $\begin{array}{l} C(NHAc)\cdot CMe{:}C\cdot N \\ \| \qquad\qquad\qquad\quad | \\ CH\text{———}CPr{:}C\cdot O \end{array}\!\!>\!CPh$, obtained by treating amidobenzamidothymol with acetic anhydride, crystallises in white needles melting at 207—208°. On treating dinitrothymol with acetic anhydride, Mazzara's dinitrothymylic acetate (*loc. cit.*) is obtained.

Alcoholic potash acts on nitramidocarvacrylic benzoate, with formation of *nitramidocarvacrol*,  $\begin{array}{l} \qquad\quad CH\cdot CMe{:}C\cdot OH \\ \qquad\quad \| \qquad\qquad | \\ NH_2\cdot C\text{—}CPr{:}CNO_2 \end{array}$; this forms beautiful yellow crystals, melting at 134—135°, and, on treatment with acetic anhydride, yields *acetamidonitrocarvacrylic acetate*,



$$\begin{array}{l} \qquad\qquad CH\cdot CMe{:}C\cdot OAc \\ \qquad\qquad \| \qquad\qquad | \\ NHAc\cdot C\text{—}CPr{:}C\cdot NO_2 \end{array},$$

which crystallises in white needles, melting at 222—225°.

W. J. P.

**Action of Nitrosodimethylaniline on Trihaloïd Substituted Phenols.** By LAZAR EDELEANU and ENESCU (*Chem. Centr.*, 1895, ii, 218; from *Bul. Soc. Sci. fizice Bucur România*, **4**, 15—19).—Nitrosodimethylaniline and 1 : 3 : 5-trichlorophenol combine when mixed in light petroleum solution, forming the compound

$$NO\cdot C_6H_4\cdot NMe_2,2C_6H_2Cl_3\cdot OH,$$

which is highly unstable, melts at 90—91°, has a green colour in solution, and is readily resolved into its constituents by the action of hydrochloric acid. At the boiling point of alcohol, the above compounds yield azoxydimethylaniline. The corresponding compound from tribromophenol is deposited in bluish-violet crystals, melting at 89—90°; when boiled with alcohol, the components also yield azoxydimethylaniline. The compound from triiodophenol has not yet been obtained in a pure state. Trichlororesorcinol and nitrosodimethylaniline yield the compound $NO{\cdot}C_6H_4{\cdot}NMe_2,C_6HCl_3(OH)_2$, which is deposited from benzene in violet crystals melting at 120°.

Triiodophenol was prepared by the interaction of iodine and alkaline phenol solution. On acidifying the liquid, triiodophenol is precipitated, together with a compound which is insoluble in alkali; it is deposited from carbon bisulphide in the form of a blue powder, and melts at 215—220°; its composition has not been determined. J. B. T.

**Derivatives of Phenetidine [Paramidophenetoïl].** By LUDWIG WENGHÖFFER (*Chem. Zeit.*, 1895, **19**, 1753).—*Benzylparamidophenetoïl*, $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}C_7H_7$, is prepared by warming a mixture of benzylic chloride and paramidophenetoïl (2 mols.), and extracting the product with ether. It crystallises in leaflets, and melts at 45—46°, dissolves in alcohol, chloroform, and ether, but is insoluble in water. It dissolves without decomposition in hot sulphuric acid, and is not attacked by hot alkalis. It appears to be a valuable febrifuge.

*Parethoxyphenyloxamide*, $C_2O_2(NH{\cdot}C_6H_4{\cdot}OEt)_2$, formed by the condensation of oxalic acid and phenetidine (2 mols.) at 140—145°, crystallises in needles, and melts at 263°; it is sparingly soluble in alcohol, benzene, and chloroform, but dissolves readily in acetic acid. Hot caustic soda decomposes it into phenetidine and sodium oxalate. It does not yield an acetyl derivative, being split up into carbonic oxide and paracetamidophenetoïl when heated at 200° with acetic anhydride. It is not poisonous.

*Paramidophenetoïl mandelate* forms shining crystals, which dissolve readily in alcohol and hot water, and melt at 105°. When it is heated at 130—170°, water is eliminated, and *amygdalyl-4-amidophenetoïl*, $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CHPh{\cdot}OH$, is formed; this crystallises from 60 per cent. alcohol, in white, shining leaflets, dissolves sparingly in hot water and in ether, and melts at 140·5°. It is stable towards dilute alkalis and acids, but is decomposed by strong sulphuric acid. Both this compound and its *acetyl derivative* have antipyretic and antiseptic properties. The latter substance melts at 154°, dissolves readily in alcohol and in acetic acid, but is only sparingly soluble in ether and hot water; it is readily hydrolysed by alkalis.

Ethylic acetoacetate condenses very readily with paramidophenetoïl to form *ethylic β-phenetidylcrotonate;* this crystallises from hot methylic alcohol in glistening, white leaflets, melting at 52·5—53°, and is insoluble in water, but soluble in alcohol and ether; dilute acids decompose it into paramidophenetoïl and ethylic acetoacetate. When heated slowly, varying quantities of diparethoxyphenylcarbamide are produced, but when it is quickly heated to 225—240°, alcohol is eliminated, and the product consists almost entirely of *4′-hydroxy-4-ethoxy-2′-methylquinoline*, $OEt{\cdot}C_9NH_4Me{\cdot}OH$; this crystallises from absolute alcohol in silky, white leaflets, dissolves with difficulty in cold water and ether, more readily in hot water, and is very soluble in alcohol. It forms salts with acids, the *hydrochloride*,

$C_{12}H_{13}NO_2 \cdot HCl$, crystallising from alcohol in slender, felted needles, the *platinochloride* forming brittle, yellow crystals. It has a bitter, not unpleasant taste, and has strongly marked antipyretic properties.

A. L.

**Constitution of Aromatic Diazo-compounds and their Isomerides.** By CHRISTIAN W. BLOMSTRAND (*J. pr. Chem.*, 1896, [2], **53**, 169—197).—A discussion of the present controversy on the subject indicated in the title, with reference to the views originally offered by the author (Abstr., 1875, 571). A. G. B.

**Azophenylethyl [Benzeneazoethane] and Acetaldehydephenylhydrazone.** By EMIL FISCHER (*Ber.*, 1896, **29**, 793—797).—The work of Thiele and Heuser (this vol., i, 340) has led them to the conclusion that the complex N⁚N·CH is not capable of existence, but changes immediately into the hydrazo-form, NH·N⁚C. The author has previously described (*Annalen*, **199**, 328) benzeneazoethane, PhN⁚NEt, and has also prepared acetaldehydephenylhydrazone, and, as this is the only example of the simultaneous existence of compounds of both types, the subject has been re-investigated.

Benzeneazoethane is obtained in the manner previously described; it may also be prepared by the action of mercuric oxide on ethylphenylhydrazine; the tetrazone is removed by crystallisation, and the azo-compound, after treatment with dilute hydrochloric acid, fractionated under reduced pressure; it boils at 88—93° (20—25 mm.), and the molecular weight agrees with the formula. The characteristic odour of the compound is most apparent when it is warmed with water; it is soluble at the ordinary temperature in concentrated hydrochloric acid and in sulphuric acid (1 : 1); when warmed, the solution suddenly boils; this was previously described as effervescence; when dissolved in sulphuric acid (60 per cent. 10 parts), and the solution allowed to remain during 15 minutes at the ordinary temperature, acetaldehydephenylhydrazone is formed; the same change probably occurs in dilute acid solution as on warming with dilute sulphuric acid, the azo-compound yielding phenylhydrazine and acetaldehyde; probably acetaldehydephenylhydrazone is first produced. With dilute hydrochloric acid, the changes are more complex; phenylhydrazine is formed in comparatively small quantity, together with a considerable amount of resinous matter.

Acetaldehydephenylhydrazone, previously termed ethylidenephenylhydrazine (*Annalen*, **190**, 136 and **236**, 137) exists in two or more forms, and is most conveniently purified by distillation; it boils at 140—150° (20—30 mm.), and crystallises from alcohol (75 per cent.) at 0° in colourless, lustrous plates melting at 66—69°; after remaining some hours in a vacuum the melting point falls to 63—65°; it is stable in a vacuum over sulphuric acid, but on exposure to moist air speedily becomes yellow, then red; it is soluble in 6 parts of light petroleum (b. p. 55—75°), and then melts at 80°; whether this is a mixture of the $\beta$-form (m. p. 66—69°) with the $\alpha$-form (see below), or a distinct modification, is uncertain. The $\alpha$-modification is prepared by boiling the $\beta$-compound for a few moments in dilute alcoholic solution with a little soda; it crystallises in long, colourless prisms, melts at 98—101°, is stable in dry air, and soluble in about 20 parts of light petroleum; the yield is 60 per cent. When recrystallised, it usually retains its melting point, but, under certain conditions which have not been determined, the melting point suddenly falls to 80°. By distillation under 20 mm. pressure, the $\alpha$-compound is reconverted into the $\beta$-derivative; the distillate, when recrystallised from alcohol, melts at about 80°, but, after 24 hours, at 64—65°. Both compounds are extremely stable towards sodium amalgam, being scarcely changed even after 24 hours' action, except that the $\beta$- is converted into the $\alpha$-form. The compounds have identical molecular weights, agreeing with the formula $C_8H_{10}N_2$. J. B. T.

**Metallic Normal Diazo-salts.** By EUGEN BAMBERGER (*Ber.*, 1896, **29**, 564—577).—Hantzsch's statements (Abstr., 1895, i, 516, 664) as to the behaviour of metallic salts of diazobenzenesulphonic acid are devoid of foundation. It is not true that the mixture of the acid with 1 equivalent of a base gives off no nitrogen at 0° while it is becoming neutral, neither is it true that its power of forming azo-dyes suffers no diminution under these circumstances. Nor is it true that the neutral solution eventually loses all its nitrogen, whereas the acid by itself, or when mixed with an excess (2 equivalents) of base, loses none; as a matter of fact, the neutral solution only loses about two-thirds of its nitrogen, even at 100°, but the solution of the acid itself loses practically all its nitrogen at that temperature. Nor is it true that the solution of the salt, $SO_3Na\cdot C_6H_4\cdot N_2\cdot ONa$, requires at first only 1 equivalent of acid to neutralise it, but eventually uses up 2 equivalents if the solution is allowed to remain until the acid reaction, caused by excess of acid, has disappeared, and more acid is then added in the same way, until a permanent acid reaction is obtained. As a matter of fact, much more than 1 equivalent of acid is invariably required to produce neutrality; apparently 2 equivalents represent the amount theoretically necessary, but often rather less suffices, presumably because a partial isomerisation of the salt takes place. Hantzsch's data being thus entirely erroneous, the arguments which he bases upon them for the existence of two geometrically isomeric varieties of diazo-salts—*syn* and *anti*—in addition to the diazonium salts, fall to the ground. C. F. B.

**Diazoacetophenone.** By ANGELO ANGELI and ENRICO RIMINI (*Gazzetta*, 1895, **25**, ii, 494—497).—Angeli has shown (Abstr., 1893, i, 570) that diazoacetophenone, $CPhO\cdot CH\vdots N_2$, is formed by the action of nitrous acid on amidoacetophenone hydrochloride; an improved method for preparing this diazo-compound is now given. It separates from hot light petroleum in long, flattened, yellow crystals, having a characteristic odour; it melts without decomposition at 50°, but above this temperature, it decomposes with evolution of gas; when rapidly heated, it explodes violently, leaving a white powder which is almost insoluble in all solvents. Diazoacetophenone has all the properties of an aliphatic diazo-compound; it is fairly stable towards alkalis, but with acids readily gives up its nitrogen, and with sulphuric acid the decomposition proceeds explosively. It is readily converted into phenacyl bromide by hydrogen bromide, and yields benzoic acid when treated with sodium carbonate. W. J. P.

**Asymmetric Phenylhydrazine Derivatives.** By HANS RUPE and GEORG HEBERLEIN (*Ber.*, 1896, **29**, 622—623; compare Abstr., 1895, i, 521).—The compound of *as*-phenylhydrazidoacetanilide is decomposed by the action of concentrated sulphuric acid with formation of *1-phenyl-3-methyl-5-ketotetrahydropyridazine-4-carboxylic acid*, $NPh<\begin{smallmatrix}N:CMe\\CH_2\cdot CO\end{smallmatrix}>CH\cdot COOH$, which decomposes at 230°. Phenylhydrazine reacts with chloracetamide to form as-*phenylhydrazidoacetamide* melting at 140°. The *benzaldehyde compound* melts at 225°. The same compound may be prepared by the reduction of nitrosoanilido-acetamide by means of zinc and acetic acid. When phenylhydrazine acts on chloracetamide, a second compound is also formed; this substance is as-*phenylhydrazido-acetophenylhydrazide*,

$$NH_2\cdot NPh\cdot CH_2\cdot CO\cdot NH\cdot NHPh,$$

and melts at 178°; it is also formed when phenylhydrazidoacetamide is heated with phenylhydrazine. Its *benzaldehyde compound* melts at 196°. A. H.

**Action of Hydrazine Hydrate on the Ethylic Derivatives of some Nitrophenols. Synthesis of 2 : 4 : 6-Trinitrometethoxyphenylhydrazine.** By ATTILIO PURGOTTI (*Gazzetta*, 1895, **25**, ii, 497—504).—Picrylhydrazine is gradually deposited from an alcoholic solution of hydrazine hydrate and ethylic picrate; ethylic 2 : 4-dinitrophenol behaves similarly.

2 : 4 : 6-*Trinitrometethoxyphenylhydrazine*,

$$OEt\cdot C_6H(NO_2)_3\cdot NH\cdot NH_2,$$

prepared by mixing trinitroresorcinol ethyl ether and hydrazine hydrate in ethereal alcoholic solution, crystallises in small, yellow needles melting at 173°; it gives the iodoform reaction, and therefore contains an ethoxy-group. Its *acetyl* derivative,

$$OEt\cdot C_6H(NO_2)_3\cdot NH\cdot NHAc,$$

produced on boiling it with acetic acid, crystallises in yellow needles melting at 179°, and its *benzylidene* derivative,

$$OEt\cdot C_6H(NO_3)_3\cdot NH\cdot N{:}CHPh,$$

prepared by boiling with acetic acid and benzaldehyde, is obtained in minute yellow needles melting at 228°.

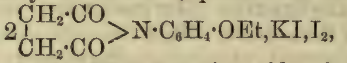
*Orthohydroxybenzylidene*-2 : 4 : 6-*trinitrometethoxyphenylhydrazine*, $OEt\cdot C_6H(NO_3)_3\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OH$, is prepared in a similar manner and forms thin, yellow, crystals melting at 217—218°. The *parahydroxy*-isomeride separates in small, red crystals melting at 231°.

*Cinnamylidene*-2 : 4 : 6-*trinitrometethoxyphenylhydrazine*,

$$OEt\cdot C_6H(NO_3)_3\cdot NH\cdot N{:}CH\cdot CH{:}CHPh,$$

forms a red crystalline powder melting at 200—201°.

W. J. P.

**Action of Iodine on Imides and Substituted Imides.** By Arnaldo Piutti (*Gazzetta*, 1895, **25**, ii, 518—527).—A *compound* of paraethoxyphenylsuccinimide, potassium iodide, and iodine, of the composition,  $2\begin{array}{l}CH_2\cdot CO\\ \vert\\ CH_2\cdot CO\end{array}\!\!>N\cdot C_6H_4\cdot OEt,KI,I_2$, is obtained by warming the constituents in dilute acetic acid solution; it forms lustrous, orthorhombic crystals which melt at 175°, and are black by reflected, but red by transmitted, light; $a:b:c = 1\cdot45320:1:0\cdot88732$. It is very soluble in alcohol or acetic acid, is dissociated into its components by water and is stable in the air. A dose of 2·5 grams administered internally to a healthy dog of average size had practically no effect; the substance has valuable antiseptic properties, and in some cases may advantageously replace iodoform in the treatment of wounds, ulcers, &c., by reason of its slow liberation of iodine.

A similar *compound* of paramethoxyphenylsuccinimide,

$$2C_2H_4{:}C_2O_2{:}N\cdot C_6H_4\cdot OMe,KI,I_2,$$

is also readily obtained; it forms monoclinic crystals resembling the preceding and melting at 150°; $a:b:c = 1\cdot42472:1:0\cdot91861$. $\beta = 87°\ 4'$. It is less stable than its homologue, being partially dissociated by acetic acid.

The *compound* with succinimide $4C_2H_4{:}C_2O_2{:}NH,KI,I_3$, crystallises in large, monoclinic, red tablets, melting at 145°;

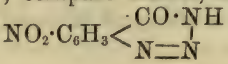
$$a:b:c = 0\cdot99278:1:0\cdot98282. \quad \beta = 74°\ 16'.$$

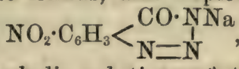
The metacetin *compound* has the composition $2C_6H_4(OMe)\cdot NHAc,I_3$, and forms red crystals soluble in acetic acid, or alcohol, but only sparingly so in water.

W. J. P.

**Decomposition of Amides and Basic Compounds.** By William Oechsner de Coninck (*Compt. rend.*, 1896, **122**, 34—35).—When treated with Leconte's reagent (sodium hypochlorite) benzamide is slightly decomposed on heating, phthalimide is readily decomposed, and salicylamide begins to decompose at the ordinary temperature. Benzanilide, hydrobenzamide, and azobenzene are not decomposed even on strongly heating; amidoazobenzene is slightly decomposed. Aniline hydrochloride is not decomposed but is converted into coloured products. Orthamidophenol remains practically unaffected even on heating, but the para-derivative is somewhat more readily attacked. The three amidobenzoic acids are decomposed in different degrees and with different velocities. Urethane is decomposed with liberation of nitrogen on gently heating, and ethylic chloride is also formed if the temperature of the liquid is raised rapidly.

C. H. B.

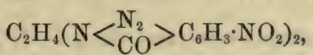
**Derivatives of Metanitrorthamidobenzamide and Metanitrorthamidobenzhydrazide.** By K. Kratz (*J. pr. Chem.*, 1896, [2], **53**, 210—225; compare Abstr., 1887, 667; 1888, 948).—*Metanitrobenzazoimide*,  $NO_2\cdot C_6H_3<\begin{array}{l}CO\cdot NH\\ \quad\quad\ \ \vert\\ N{=}N\end{array}$ $[NO_2:CONH:N_2 = 5:1:2]$,

is prepared by diazotising metanitrorthamidobenzamide; it crystallises in yellowish, silvery, quadratic laminæ, darkens at 178°, and decomposes and melts at 185°; it dissolves sparingly in cold water, and cold alcohol, but freely in the hot solvents, and in chloroform and glacial acetic acid; ether dissolves it sparingly, benzene not at all; alkalis dissolve it easily, and it is precipitated from the solutions by acids; it is feebly acid to litmus, and explodes when heated on platinum. The *sodium* salt,  $NO_2\cdot C_6H_3<\begin{matrix}CO\cdot NNa\\ \quad|\\ N{=}N\end{matrix}$, is precipitated by adding ether to mixed alcoholic solutions of the nitrobenzazoimide and sodium; it forms yellowish needles, easily soluble in alcohol and water. The *silver* salt is described.

*Metanitramidobenzomethylamide*, $NO_2\cdot C_6H_3(NH_2)\cdot CO\cdot NHMe$, prepared by the action of methylamine on nitroisatoic acid in water (compare Kolbe, Abstr., 1885, 665), crystallises in yellow needles, melts and partly decomposes at 230—231°, and dissolves freely in water, hot glacial acetic acid, and alcohol, sparingly in chloroform, and not at all in benzene. The *methylic* salt of metanitrobenzazoimide may be prepared either by diazotising this methylamide, or by heating sodium metanitrobenzazoimide with methylic iodide; it crystallises in yellow laminæ, melts at 199° and dissolves sparingly in ether, but freely in warm water, warm alcohol, chloroform, glacial acetic acid, and warm methylic alcohol.

*Metanitrorthamidobenzethylamide* is prepared like the methylamide; it crystallises in long, yellow, brittle needles, becomes brown and melts at 156°, and dissolves sparingly in water and chloroform, more freely in dilute alcohol, and freely in glacial acetic acid. When diazotised, it yields the *ethylic* salt of metanitrorthobenzazoimide; this crystallises in yellowish tables, melts at 105°, and dissolves sparingly in water, but freely in alcohol and glacial acetic acid.

*Metanitrorthamidobenzethylenamide*, $C_2H_4[NH\cdot CO\cdot C_6H_3(NH_2)\cdot NO_2]_2$, from ethylenediamine and nitroisatoic acid, crystallises from hot glacial acetic acid in yellow laminæ, becomes brown at 275°, and melts above 290°. *Ethylenic metanitrorthobenzazoimide*,

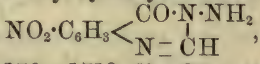


$$C_2H_4(N<\genfrac{}{}{0pt}{}{N_2}{CO}>C_6H_3\cdot NO_2)_2,$$

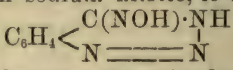
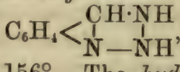
is obtained by diazotising the ethylenamide; it crystallises from glacial acetic acid in brown laminæ, and melts above 290°.

*Metanitrorthamidobenzanilide*, $NO_2\cdot C_6H_3(NH_2)\cdot CO\cdot NHPh$, from aniline and nitroisatoic acid, forms yellow, silky needles, melts at 203°, and dissolves sparingly in water, alcohol, chloroform, and amylic alcohol, but not at all in ether and benzene; *phenylmetanitrorthamidobenzazoimide* crystallises in yellowish laminæ, and melts at 190°.

The foregoing benzazoimides yield orthamidobenzoic acid when heated with strong caustic potash, metanitrorthochlorobenzoic acid when heated with strong hydrochloric acid at 120—130°, and metanitrosalicylic acid when heated with dilute sulphuric acid.

*Metanitrorthobenzhydrazide*, $NO_2\cdot C_6H_3(NH_2)\cdot CO\cdot N_2H_3$, is prepared by dissolving hydrazine sulphate with the appropriate quantity of alkali in 10 times its weight of water, and adding nitroisatoic acid in small portions; it crystallises in yellow needles and decomposes, without melting, between 214° and 218°; it dissolves easily in alcohol and water, but not in chloroform or ether; glacial acetic acid and nitric acid dissolve it somewhat easily. The *benzylidene* derivative, $NO_2\cdot C_6H_3(N:CHPh)\cdot CO\cdot NH\cdot N:CHPh$, crystallises in yellow tables, and melts at 224—225°. When heated with anhydrous formic acid, the hydrazide yields a formyl derivative which is decomposed by hydrolysis into *anhydroformylmetanitrorthamidobenzhydrazide*,  $NO_2\cdot C_6H_3<\begin{array}{l}CO\cdot N\cdot NH_2\\ \qquad\ \ |\\ N = CH\end{array}$, which crystallises in yellow needles, melts at 170—171°, dissolves sparingly in chloroform and ether, and easily in hot water and hot alcohol, and has the reactions common to alkaloïds. A. G. B.

**Derivatives of Orthamidobenzonitrile.** By JOHANNES PINNOW and C. SÄMANN (*Ber.*, 1896, **29**, 623—632).—*Orthacetamidobenzonitrile*, obtained by the action of acetic anhydride on amidobenzonitrile, crystallises in long, silky needles, melting at 133° (uncorr.). *Orthobenzamidobenzonitrile* forms needles melting at 216° (uncorr.). *Orthocyanophenylcarbamide* is formed by the action of potassium isocyanate on the hydrochloride of the nitrile; it crystallises in plates, which do not melt below 300°, and is insoluble in all organic solvents except alcohols. *Orthocyanodiphenylcarbamide* is prepared by the combination of the nitrile with phenylcarbimide, and crystallises in plates, which melt at 194° (uncorr.). *Orthocyanothiocarbanilide* is a crystalline powder, which does not melt below 300°. *Orthodicyanothiocarbanilide* crystallises in yellowish plates, which also do not melt below 300°.

*Orthamidobenzenylamidoxime*, $NH_2\cdot C_6H_4\cdot C(NH_2):N\cdot OH$, is obtained by the action of hydroxylamine hydrochloride on a solution of amidobenzonitrile in alcoholic sodium ethoxide; it crystallises in lustrous plates, melts at 84—85°, and yields a *picrate*, which melts at 182°. The *hydrochloride* is readily soluble in water, and crystallises in slender needles. When it is treated with sodium nitrite, it is converted into *ketodihydrophenotriazinoxime*,  $C_6H_4<\begin{array}{l}C(NOH)\cdot NH\\ \qquad\qquad\ \ |\\ N = \!= \!= N\end{array}$; this crystallises from alcohol with 1 mol. of the solvent in slender, light yellow needles, which melt at 181° and lose alcohol when dried. The *hydrochloride* melts at 151° and readily decomposes. The compound is both a weak acid and a weak base. When reduced with stannous chloride and hydrochloric acid, it is converted into n-*dihydro-β-phenotriazine*,  $C_6H_4<\begin{array}{l}CH\cdot NH\\ |\qquad |\\ N - NH\end{array}$, which crystallises in lustrous plates and melts at 156°. The *hydrochloride* forms thick needles and melts at 169°, whilst the *sulphate* melts at 225°, and the *picrate* at 241°. The base yields a *diacetyl derivative*, which crystallises in needles, melts at 179°, and is decomposed by acids, with re-formation of the original base. The *dibenzoyl derivative* also crystallises in needles and melts at 182°. The base does not give the isonitrile reaction. When orthamidobenzenylamidoxime is heated with acetic anhydride, it is converted into *acetorthamidobenzenylazoximethenyl*, $C_{11}H_{11}N_3O_2$, which crystallises in slender needles, melting at 96°. When treated with hydrochloric acid, the corresponding base, *orthamidobenzenylazoxime-ethenyl*, $C_9H_9N_3O$, is formed, which crystallises in short needles and melts at 87°. The *hydrochloride* melts at 178—179°. The base readily undergoes the diazo-reaction, and the resulting diazo-salt reacts with β-naphthylamine to form a colouring matter, $C_{19}H_{15}N_5O$, which crystallises in scarlet-red plates and melts at 153—154°. When orthamidobenzonitrile hydrochloride is treated with sodium nitrite and hydrochloric acid, it is converted into *orthodicyanodiazo-amidobenzene*, $C_{14}H_9N_5$, which crystallises in small, yellow needles, melting at 133°. When the acid filtrate from this compound is brought into a boiling solution of cupropotassium cyanide, a small quantity of *phthalonitrile*, $C_6H_4(CN)_2$, is formed; this substance crystallises in slender needles, and melts at 141°. A. H.

**Halogen Additive Products of the Anilides.** By HENRY L. WHEELER and P. T. WALDEN (*Amer. Chem. J.*, 1896, **18**, 85—90).—The substances previously described by Wheeler (this vol., i, 23) as dibromine additive products of metanitracetanilide were mixtures of the perbromides, $(NO_2{\cdot}C_6H_4{\cdot}NHAc)_2,HBr,Br_2$ and

$$(NO_2{\cdot}C_6H_4{\cdot}NHAc)_2,HBr,Br_4.$$

The hydrobromide, $(NO_2{\cdot}C_6H_4{\cdot}NHAc)_2HBr$, from metanitracetanilide, yields a *dibromide*, crystallising in orange-coloured, flat prisms, a *tetrabromide*, forming deep orange prisms, and a *hexabromide*, crystallising in brick-red needles.

The *hydrobromide*, $(C_6H_4Br{\cdot}NHAc)_2,HBr$, from parabromacetanilide, crystallises in colourless needles; it gives a *dibromide*, forming flat, orange prisms, and a *tetrabromide*, crystallising in deep orange-coloured prisms.

The *hydriodide*, $(NHPhAc)_2,HI$, from acetanilide, forms shining, colourless scales; it gives a *diiodide*, in ruby-red crystals, and a *tetriodide*, crystallising in lustrous, deep, reddish-brown prisms.

These compounds are strictly analogous to the perhaloïds $CsBr,Br_2$, $CsI,I_4$, and $NH_4Br,Br_2$. In general, when bromine is mixed with an anilide under conditions which permit of the formation of hydrogen bromide, this acid unites with the anilide to form an ammonium salt, and this salt then unites with bromine. Bromine free from hydrogen bromide has, however, no action on metanitracetanilide or parabromacetanilide. A. E.

**Action of Oxalic and Malonic acids on Paramidophenol and its Ethers.** By E. CASTELLANETA (*Gazzetta*, 1895, **25**, ii, 527—542).—Piutti has shown (this vol., i, 223) that paramidophenol and phthalic or succinic acid react in molecular proportion, yielding substituted imides; the reaction between oxalic or malonic acid and paramidophenol or its ethers, however, proceeds in accordance with the equation $2R''(COOH)_2 + 3C_6H_4(NH_2){\cdot}OR' =$

$$3H_2O + R''(CO{\cdot}NH{\cdot}C_6H_4{\cdot}OR')_2 + COOH{\cdot}R''{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OR',$$

a substituted diamide and a mono-substituted monamido-acid being produced.

*Diparahydroxyphenyloxamide*, $C_2O_2(NH\cdot C_6H_4\cdot OH)_2$, is prepared by melting oxalic acid and the amidophenol together, or by boiling the amidophenol with ethylic oxalate; it forms small crystals, which sublime at 280°. Its *diacetyl* derivative is formed on boiling it with acetic anhydride, and crystallises in scales subliming at 260°.

*Diparamethoxyphenyloxamide*, $C_2O_2(NH\cdot C_6H_4\cdot OMe)_2$, from paranisidine and oxalic acid, crystallises in scales melting at 254°. It is accompanied by *paramethoxyphenyloxamic acid*,

$$COOH\cdot CO\cdot NH\cdot C_6H_4\cdot OMe,$$

which crystallises in white prisms, melting at 166—167°; its *ethylic* salt crystallises in colourless scales, melting at 108°.

On extracting with alcohol the product obtained on heating oxalic acid with phenetidine, *diparaethoxyphenyloxamide* remains undissolved, and forms a micro-crystalline powder; it is accompanied by *parethoxyphenyloxamic acid*, which crystallises in red scales, melting and decomposing at 180—181°, and gives an *ethylic* salt, crystallising in iridescent scales melting at 110—111°.

The following compounds are obtained by heating malonic acid, or its ethylic salt, with paramidophenol and its alkylic derivatives.

*Diparahydroxyphenylmalonamide*, $CH_2(CO\cdot NH\cdot C_6H_4\cdot OH)_2$, crystallises in colourless scales, melting at 235° with decomposition, and yields a crystalline *diacetyl* derivative, melting at 210°.

*Diparamethoxyphenylmalonamide* forms white needles, melting at 232—233°; *paramethoxyphenylmalonamic acid*,

$$COOH\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot OMe,$$

crystallises in colourless scales, melting and decomposing at 143°, whilst its *ethylic* salt crystallises in needles, melting at 73°.

*Diparaethoxyphenylmalonamide* crystallises in colourless needles, melting at 233—234°; *paraethoxyphenylmalonamic acid* crystallises in colourless scales, melting at 143° with decomposition, and yields an *ethylic* salt, which forms scales, melting at 109°. W. J. P.

**Derivatives of Cinnamaldehyde.** By Max Scholtz (*Ber.*, 1896, **29**, 613—615).—Cinnamaldehyde condenses with methyl ethyl ketone in the presence of sodium ethoxide; the compound formed, $C_{13}H_{14}O$, melts at 108—110°, its yellow *oxime* at 142—143°.

Cinnamylideneacetone, from cinnamaldehyde and acetone, condenses further with benzaldehyde in dilute alcoholic soda solution to a yellow compound, $CHPh{:}CH\cdot CH{:}CH\cdot CO\cdot CH{:}CHPh$, melting at 106°, the yellow *oxime* of which melts at 127—128°. C. F. B.

**Synthesis of Vanillin.** By A. Fajans (*Chem. Centr.*, 1895, ii, 567; from *Ber. Österr. Chem. Ges.*, 1895, **17**, 40).—By the action of liquid carbonic anhydride at 120° on sodiorthomethoxyhydroxybenzene, a monocarboxylic acid is formed, but, at 180°, the dicarboxylic acid [$(COOH)_2 : OH : OMe = 1 : 5 : 2 : 3$] is produced, and, when treated with hydrochloric acid under pressure, it yields methylic chloride and isonorhemipinic acid; when heated alone at 277°, vanillic acid [$OH : OMe : COOH = 4 : 3 : 1$] is produced, and this is converted into vanillin by the action of chloroform and potash.

J. B. T.

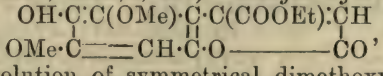
**Synthesis in the Gentisin Series.** By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Monatsh.*, 1895, **16**, 919—925; compare Abstr., 1894, 340).—The monomethyl ether of quinolcarboxylic acid [$OH : COOH : OMe = 1 : 2 : 4$] is readily obtained from the latter by the action of alkali and methylic iodide. When cautiously distilled with phloroglucinol in presence of acetic anhydride, it yields a yellow sublimate, separable, by means of dilute soda, into two parts. The highly coloured, insoluble portion is the sodium derivative of an acid, which crystallises in broad, yellow needles and melts at 167°; the latter is identical with the dimethyl ether of trihydroxyxanthone [$OH : (OMe)_2 = 1 : 3 : 3'$], and is probably produced by the partial methylation of the monomethyl ether by the methylic alcohol formed in the hydrolysis of another portion. Trihydroxyxanthone was detected in the portion of the sublimate soluble in soda, and was accompanied by its monomethyl ether, gentisin, which was isolated by means of its diacetyl derivative.

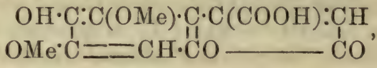
The above synthesis of gentisin does not afford a complete proof of the constitution of that substance, as the possibility of its production from the trihydroxyxanthone, by methylation, is not excluded.

A. L.

**The Behaviour of Alkaline Solutions of Ethylic Formylphenylacetate towards Acids.** By WILHELM WISLICENUS (*Ber.*, 1896, **29**, 742—743; compare Abstr., 1895, i, 366).—The liquid isomeride of ethylic formylphenylacetate, which gives a bluish-violet coloration with ferric chloride, is the weaker acid of the two, and has the constitution OH·CH:CPh·COOEt, whilst the solid isomeride has the constitution CHO·CHPh·COOEt, and is the stronger acid. Either of the two isomerides can be obtained from the same alkaline solution by varying the treatment adopted. If carbonic anhydride be passed in, the liquid isomeride is precipitated, whilst, if the solution be treated with an excess of sulphuric acid, the solid form is obtained (compare Hantzsch and Schultze, this vol., i, 353). This method appears to be a general one for obtaining isomerides of different acidity.

A. H.

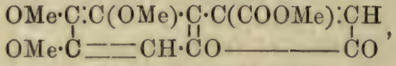
**Fraxetin.** By PIETRO BIGINELLI (*Gazzetta*, 1895, **25**, ii, 365—373; compare Abstr., 1895, i, 419).—*Ethylic hydroxydimethoxycoumarin-β-carboxylate*,  $\begin{array}{l}\mathrm{OH{\cdot}C{:}C(OMe){\cdot}C{\cdot}C(COOEt){:}CH} \\ \quad | \qquad\qquad\qquad\quad \| \qquad\qquad\qquad\qquad | \\ \mathrm{OMe{\cdot}C{=\!=\!=}CH{\cdot}C{\cdot}O{-\!-\!-\!-\!-}CO}\end{array}$, is formed on gradually adding a solution of symmetrical dimethoxyquinol in ethylic oxalacetate to concentrated sulphuric acid; on pouring the product on to ice, the salt separates, and is ultimately obtained in prisms melting at 199—200°. It is sparingly soluble in water or ether, and dissolves in alkalis, but not in alkali carbonates. On acidifying its alkali solution with hydrochloric acid, the corresponding *acid*,



$$\begin{array}{l} \mathrm{OH{\cdot}C{:}C(OMe){\cdot}C{\cdot}C(COOH){:}CH} \\ \mathrm{OMe{\cdot}C{=\!=}CH{\cdot}CO \text{———} CO} \end{array},$$

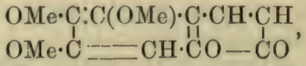
is deposited; it crystallises with $2H_2O$ in yellow needles, melting and decomposing at 248—250°. These lose their water below 100°, and are soluble in water or alcohol, giving solutions which are yellow when cold, and red when hot. The anhydrous acid is red, but on dissolving it in hot hydrochloric acid and allowing the solution to cool, two *modifications* of the acid, containing $H_2O$ and $\frac{1}{2}H_2O$ respectively, are deposited; these crystallise in yellow needles, which do not turn red or lose water on heating, and, when precipitated from their alkali solution by a mineral acid, yield the modification containing $2H_2O$.

*Methylic trimethoxycoumarin-β-carboxylate*,



$$\begin{array}{l} \mathrm{OMe{\cdot}C{:}C(OMe){\cdot}C{\cdot}C(COOMe){:}CH} \\ \mathrm{OMe{\cdot}C{=\!=}CH{\cdot}CO \text{————} CO} \end{array},$$

is obtained by heating a solution of the above acid in methylic alcohol with potash and methylic iodide; after distilling off the solvents, washing with water, and crystallising from alcohol, the salt is obtained in white laminæ, melting at 105—106°. It is sparingly soluble in alkalis, and, when boiled with potash, undergoes hydrolysis, yielding *trimethoxycoumarin-β-carboxylic acid*, which is precipitated from the solution on adding an acid; it crystallises in yellow needles or scales, melting at 209°, and, like the preceding acid, decomposes above its melting point, with evolution of carbonic anhydride. When distilled with iron powder, it yields *trimethoxycoumarin*,



$$\begin{array}{l} \mathrm{OMe{\cdot}C{:}C(OMe){\cdot}C{\cdot}CH{\cdot}CH} \\ \mathrm{OMe{\cdot}C{=\!=}CH{\cdot}CO{-}CO} \end{array},$$

an isomeride of dimethylfraxetin; this crystallises in white needles melting at 74—75°, and is very soluble in alcohol; it is precipitated from its potash or soda solution by carbonic anhydride.

W. J. P.

**Optical Activity of Tannin.** By Hugo Schiff (*Gazzetta*, 1895, **25**, ii, 437—442).—The author confirms Gunther's statement (*Ber. d. pharm. Ges.*, **5**, 172), that tannin has a small dextrorotation; he therefore proposes to modify the received constitutional formula of gallic and tannic acids, the latter being represented as a ketonic compound, so that they shall be represented as containing asymmetric carbon atoms. W. J. P.

**Ethylic Trinitrophenylmalonate.** By C. Loring Jackson and C. A. Soch (*Amer. Chem. J.*, 1896, **18**, 133—141).—*Ethylic trinitrophenylmalonate* (*picrylmalonate*) is readily obtained by mixing a strong, cold, benzene solution of picryl chloride with an alcoholic solution of ethylic sodiomalonate; it forms long, white, rectangular plates, melting at 58°, and giving pink solutions in most organic solvents. The *sodium derivative*, $C_6H_2(NO_2)_3{\cdot}CNa(COOEt)_2$, forms dark red crystals, and, when dry, explodes on warming. Its aqueous solution gives red precipitates, with solutions of magnesium, calcium, barium, nickel, lead, and silver salts, and a yellow precipitate with manganese salts.

The *bromo-derivative*, $C_6H_2(NO_2)_3 \cdot CBr(COOEt)_2$, crystallises in white, nearly square, striated plates, melting at 85—86°; its alcoholic solution has only a faint pink colour. Sodium carbonate has no action, neither has sodium hydroxide in the cold, but on heating, a red solution is obtained, bromine being first removed. *Ethylic bromodinitrophenylbromomalonate*, $C_6H_2Br(NO_2)_2 \cdot CBr(COOEt)_2$, was obtained by the action of bromine in excess on a solution of ethylic bromodinitrophenylmalonate (Abstr., 1888, 1091) in glacial acetic acid. It crystallises from alcohol in long, white prisms, melting at 72—73°. It is insoluble in water, but on long boiling is broken up, the bromine in the side-chain being removed. Strong sodium and ammonium hydroxides have a similar effect on warming, although there is but little action in the cold. A E.

**The Action of Ortho- and Para-nitrobenzylic Chlorides on Ethylic Sodiomalonate and some Analogous Compounds.** By ARNOLD REISSERT (*Ber.*, 1896, **29**, 633—638).—Orthonitrobenzylic chloride reacts with ethylic sodiomalonate to form ethylic orthodinitrodibenzylmalonate, a portion of the ethylic malonate being regenerated. When twice the molecular proportion of ethylic sodiomalonate is used, however, about three-fifths of the product consists of *ethylic orthonitrobenzylmalonate.* The pure compound is a light red oil, which does not solidify in a freezing mixture, and cannot be distilled without undergoing decomposition. When heated with hydrochloric acid at 140—150°, it yields orthonitro-$\beta$-phenylpropionic acid (Gabriel and Zimmermann, *Ber.*, **13**, 1680). Paranitrobenzylic chloride behaves towards ethylic sodiomalonate in a similar manner to the ortho-compound. The mono-substitution derivative has already been described by Lellmann and Schleich (Abstr., 1887, 490). *Ethylic orthoparadinitrodibenzylmalonate* is obtained by the action of orthonitrobenzylic chloride on ethylic paranitrobenzylsodiomalonate in alcoholic solution; it crystallises in white needles, which melt at 103·5°, and, when heated with hydrochloric acid at 180°, yields *orthoparadinitrodibenzylacetic* acid, which was previously obtained by the author as a bye-product in the preparation of diorthonitrobenzylacetic acid (Abstr., 1894, i, 626). Orthonitrobenzylic chloride reacts with ethylic sodioacetoacetate to form *ethylic orthodinitrodibenzylacetoacetate*, which crystallises in soft needles melting at 103°. With ethylic cyanoacetate, orthonitrobenzylic chloride yields a mixture of the liquid mono-substitution derivative with *ethylic orthodinitrodibenzylcyanoacetate*, which crystallises in large prisms, and melts at 81°. Orthonitrobenzylic chloride further reacts with ethylic sodiomethanetricarboxylate, forming derivatives of ethylic malonate, a carboxyethyl group being eliminated. A. H.

**Sulphoparabromobenzoic Dichloride.** By CARL BÖTTINGER (*Chem. Zeit.*, 1895, **19**, 1684; compare Abstr., 1878, 729).—The dichloride of sulphoparabromobenzoic acid may be obtained in a pure state by the following method.

The normal potassium salt of the acid is covered with light petroleum and warmed in a flask with the calculated quantity of powdered phosphorus pentachloride, and the solution of mixed chlorides thus obtained is separated by filtration from potassium chloride, mixed with an equal volume of ether, and repeatedly shaken with water to remove phosphorus oxychloride. On evaporation of the ether, the pure dichloride is deposited in beautiful, oblique, four-sided plates. It melts at 59°, and is readily decomposed by water.

In the preparation of the diethylic salt, *ethylic hydrogen sulphoparabromobenzoate* is also produced, and is found in the mother liquors from the former substance. It is a beautifully crystalline compound melting at 157—162°, and is very soluble in water. Both this and the diethylic salt, when heated, yield ethylic parabromobenzoate. As the amidoethylic salt, melting at 128°, formed, together with the corresponding amido-acid, by the action of alcoholic ammonia on the dichloride (*loc. cit.*), gives no trace of ethylic parabromobenzoate on decomposition, it would appear that it is the ethylic salt of parabromobenzamidosulphonic acid. This conclusion is supported by other circumstances.

The author has been unable to obtain a diamide from the above dichloride, as Ullmann stated that he did from the corresponding chloro-compound (Abstr., 1895, i, 181). A. L.

**The Action of Phosphorus Pentachloride on Parasulphaminebenzoic acid.** By IRA REMSEN, R. N. HARTMAN, and ARTHUR M. MUCKENFUSS (*Amer. Chem. J.*, 1896, **18**, 150—170).—It has been shown that phosphorus pentachloride and benzoic sulphinide, gives orthochlorocyanobenzene (Remsen and Dohme, Abstr., 1889, 992), whilst parasulphaminebenzoic acid yields parachlorocyanobenzene. A further investigation of the latter reaction has now been made, and shows that, below 70°, *phosphochloroparasulphaminebenzoic chloride*, $COCl\cdot C_6H_4\cdot SO_2\cdot NPCl_3$, is formed; at 146—200° this gives off phosphoric oxychloride, leaving *paracyanobenzenesulphonic chloride*, $CN\cdot C_6H_4\cdot SO_2Cl$; and at 205° the latter breaks up into $SO_2$ and parachlorocyanobenzene, $C_6H_4\cdot Cl\cdot CN$.

Phosphochloroparasulphaminebenzoic chloride crystallises in transparent prisms, which quickly turn white on exposure to air, and absorb moisture eagerly, giving off hydrogen chloride. It melts at 82°, and dissolves in warm water, forming parasulphaminebenzoic acid.

Paracyanobenzenesulphonic chloride crystallises in large, rhombic, transparent prisms, melts at 111—112°, and sublimes in rough, white needles. With aqueous ammonia, an amide is formed which, on treatment with alkalis, or on heating with water in a sealed tube, is converted into parasulphaminebenzoic acid.

When the chloride is heated with water at 200° in a sealed tube, it yields the acid ammonium salt of parasulphobenzoic acid, which was identified by transforming it into the barium salt (Remsen, this Journal, 1876, i, 257). On simply boiling with water, paracyanobenzenesulphonic chloride is converted into the corresponding *acid*,

$CN·C_6H_4·SO_3H$ [1 : 4], which separates from the concentrated aqueous solution in small, prismatic crystals. Owing to its great solubility, it could not be purified sufficiently for analysis. The *barium* and *potassium* salts are described. *Paracyanobenzenesulphonamide*, $CN·C_6H_4·SO_2NH_2$, crystallises from hot water in long, lustrous prisms melting at 168—169°. *Paracyanobenzenesulphonanilide*,

$$CN·C_6H_4·SO_2·NHPh,$$

crystallises from alcohol in long, prismatic plates, and from benzene in fine, flat, satiny needles melting at 112°. Alkalis decompose it, on boiling, with evolution of ammonia, and from the alkaline solution acids precipitate *parasulphanilidobenzoic acid* as a white, flocculent mass. This may be crystallised from alcohol in feathery plates melting and partially decomposing at 252—253°. The *barium* salt, with $5H_2O$, and the *potassium* salt, with $2H_2O$, are described.

*Paracyanobenzenesulphorthotoluidide*, $CN·C_6H_4·SO_2·NH·C_7H_7$, forms prisms melting at 122—123°. *Orthotoluidoparasulphobenzoic acid*, $COOH·C_6H_4·SO_2·NH·C_7H_7$, resembles the anilido-acid, and crystallises from alcohol in white, flat needles melting and decomposing at 246—247°. The *barium* salt crystallises, with $5H_2O$, in minute, white plates, or with $H_2O$ in larger prismatic plates. *Paracyanobenzenesulphometatoluidide* forms white prisms melting at 128°. *Metatoluidoparasulphobenzoic acid* crystallises from alcohol in white, shining plates or leaflets melting at 241—242°; the *barium salt*, with $5H_2O$, forms long prisms, or with $3H_2O$, lustrous, prismatic plates. *Paracyanobenzenesulphoparatoluidide* crystallises in rhombic prisms melting at 151—152°, and dissolves unchanged in alkalis, but, on heating the solution, *paratoluidoparasulphobenzoic acid* is obtained; this forms beautiful, white plates or leaflets melting and decomposing at 282—283°. The *barium salt*, with $H_2O$, crystallises in small, white prisms.

On heating a mixture of parasulphaminebenzoic acid and phosphorus pentachloride, *parachlorcyanobenzene* distils as an oil which soon solidifies. It is deposited from hot alcohol in long, prismatic needles which gradually dissolve on standing, and are replaced by new crystals much shorter and thicker than the first. The melting point is 93—94°. A. E.

**Dissociation of Diazosulphonates.** By EUGEN BAMBERGER (*Ber.*, 1896, **29**, 608—610).—Hantzsch has calculated his cryoscopic results (Abstr., 1895, i, 664) wrongly. Properly calculated, they lead to conclusions the opposite of those which he states. The anti-salt exhibits *increasing*, and not decreasing, dissociation with increase of concentration. And, further, the iso- (anti-) salt appears more dissociated, hydrolytically, than is the normal (syn-) salt—which is contrary to experience. C. F. B.

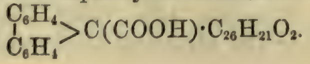
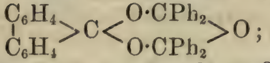
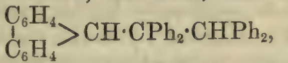
**The Stereoisomeric Salts of Diazosulphanilic acid.** By DIMITER GERILOWSKI and ARTHUR R. HANTZSCH (*Ber.*, 1896, **29**, 743—755; compare Abstr., 1895, i, 664).—The electrical conductivity of solutions of the anti-sodium salt prepared from paradiazosulphanilic acid show that at 0°, $\mu = 80{\cdot}2$ ($v = 32$), $97{\cdot}4$ ($v = 1024$), the increase in $\mu$ between the values $v = 32$ and $v = 1024$ being, therefore, 17·2. This agrees well with the numbers obtained for other sodium salts of dibasic acids which are not hydrolysed by the water of dissolution; sodium succinate, for example, shows an increase of 18·76 at the same temperature. The syn-salt gives the values $\mu = 81$ ($v = 32$), and $\mu = 112$ ($v = 1024$); the difference in this case being 31. This shows that the syn-salt, which possesses the normal structure, is hydrolysed to a larger extent than the anti-salt; so that the normal diazo-group must be considered to be of a less acid character than the iso-group. The dissociation of the two salts undergoes almost the same diminution when a molecule of caustic soda is added. These results are considered by the authors to prove that the two salts have a similar constitution, and that the normal salt cannot have the constitution $NaSO_3{\cdot}C_6H_4{\cdot}N(ONa){:}N$, since, in that case, it would be almost as completely dissociated as caustic soda, for which $\mu = 128$ when $v = 32$.

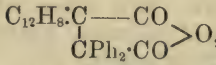
The change from diazonium compound to syn-diazo-compound, which occurs when diazoniumsulphanilic acid is dissolved in caustic soda, appears to take place with great rapidity, as the solution shows the conductivity of the syn-salt as soon as it is prepared. The reverse change takes place very rapidly when a mineral acid is added to the alkaline solution. The change from syn- to anti-salt occurs extremely slowly at 0°, and does not interfere with the determination of the conductivity.

A comparison of the oximes shows that the syn-oxime is a stronger acid than the anti-oxime. A. H.

**Synthesis of Diphenylene Ketone and its Derivatives.** By Wilhelm Staedel (*Ber.*, 1896, **29**, 615).—Syntheses of this kind, which Pschorr proposes to attempt (this vol., i, 303), have already been carried out by the author (Abstr., 1895, i, 147, 233) and others.

C. F. B.

**Action of Sulphuric acid on Benzilic acid.** By Heinrich C. Klinger and Carl Lonnes (*Ber.*, 1896, **29**, 734—741; compare Abstr., 1889, 885).—Four products are formed by the action of cold concentrated sulphuric acid on benzilic (diphenylglycollic) acid or its air-dried potassium salt, a mixture of these being precipitated when the product of the action is diluted with ice. When the drained mass is dissolved in benzene, and this solution shaken with potash, a sulphonic acid is dissolved out together with an acid of the formula $C_{27}H_{20}O_3$; the potassium salt of a third acid, $C_{40}H_{30}O_4$, separates in needles, whilst the benzene solution retains the fourth substance, diphenyldiphenylenesuccinic anhydride. The *acid*, $C_{40}H_{30}O_4$, melts at 208—210°, and forms a *potassium salt*, which is almost insoluble in water; the *methylic salt* melts at 208—209°. When the acid is reduced with hydriodic acid at 160—170°, it yields diphenyleneacetic acid and diphenylmethane, and has, therefore, probably the constitution  $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>C(COOH){\cdot}C_{26}H_{21}O_2$. On oxidation with chromic acid, the acid is converted into *tetraphenyldiphenylenetrioxymethylene*,  $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}C{<}\genfrac{}{}{0pt}{}{O\cdot CPh_2}{O\cdot CPh_2}{>}O$; this crystallises in plates which have a golden lustre, and melt at 205—206°. When its solution in acetic acid is boiled with hydriodic acid, it yields *tetraphenyldiphenylenepropylene oxide*, $C_{39}H_{28}O$, which crystallises in well-developed yellow prisms, melts at 202—203°, and is re-converted into the trioxymethylene compound by chromic acid. Complete reduction converts the substance into diphenylmethane and fluorene. Hydriodic acid at 110—120°, however, converts it into *tetraphenyldiphenylenepropane*,  $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}CH\cdot CPh_2\cdot CHPh_2$, which is also formed in small quantity when the acid $C_{40}H_{30}O_4$ is distilled with soda-lime, and when the propylene oxide is treated with zinc dust and acetic acid, in the latter case it is accompanied by two compounds, of the formula $C_{39}H_{30}O$, melting at 186° and 223° respectively. It crystallises in long, white needles, and melts at 205°. When the potassium salt of the acid is heated at 120—150° with an indifferent solvent, it yields potassium carbonate and a substance of the formula $C_{39}H_{30}O_2$, which crystallises well, melts at 220° and is converted by oxidation into the trioxymethylene compound.

*Diphenyldiphenylenesuccinic anhydride*,  $\genfrac{}{}{0pt}{}{C_{12}H_8{:}C\text{---}CO}{CPh_2\cdot CO}{>}O$, forms well-developed crystals melting at 256°. Its solution in alcoholic potash deposits the corresponding acid on acidification, but this passes into the anhydride on drying. Hydriodic acid converts it into diphenyleneacetic and diphenylacetic acids. When the anhydride is heated with aqueous potash at 150° it forms *diphenyldiphenylenepropionic acid*, $C_{12}H_8{:}CH\cdot CPh_2\cdot COOH$, which crystallises in white plates, and melts and decomposes at 239°, whilst, on reduction, it yields *diphenyldiphenylenethane*, $C_{12}H_8{:}CH\cdot CHPh_2$, which forms white needles melting at 217°. On oxidation, the acid is converted into benzophenone fluorene ketone and diphenyldiphenylenethylene, $C_{12}H_8{:}C{:}CPh_2$, which melts at 225—226°. This hydrocarbon is colourless, but yields deep, yellow-coloured solutions, and is identical with the hydrocarbon obtained from benzophenone chloride and fluorene (Kaufmann, this vol., i, 242).

The *acid* $C_{27}H_{20}O_3$ is an amorphous, white mass, and in alkaline solution readily oxidises on exposure to the air, forming a substance of the formula $C_{26}H_{18}O_2$; this crystallises in plates with a golden lustre, and melts at 175°. This is unaffected by most reagents, but is reduced by hydriodic acid to fluorene and diphenylmethane; on moderate reduction, it forms a compound, $C_{26}H_{18}O$, which is also yellow, and melts at 157°.

When it is reduced, it yields a hydrocarbon $(C_{13}H_{10})_n$, which melts at 149—150°, and is perhaps *as*-diphenyldiphenylenethane.

The molecular weights of the various compounds described were, almost without exception, determined by the cryoscopic method.

A. H.

**Acid Rosanilines.** By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1896, [3], **13**, 581—583).—A controversial reply to Rosenstiehl (Abstr., 1895, i, 667). JN. W.

**Ammoniated Derivatives of Hexamethyltriamidotriphenylmethane.** By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1896, [3], **13**, 546—581; compare Abstr., 1895, i, 377, 476).—Hexamethyltriamidotriphenylmethane, $CH(C_6H_4{\cdot}NMe_2)_3$, combines readily with methylic iodide in the cold to form a *trimethiodide*, $CH(C_6H_4{\cdot}NMe_3I)_3$, crystallising in colourless needles, and melting and decomposing at 188°; it is rather unstable, gradually losing methylic iodide when kept. The methiodide is converted by caustic alkalis, or better, by moist silver oxide, into the corresponding *hydroxide*,

$$CH(C_6H_4{\cdot}NMe_3{\cdot}OH)_3$$

which, like the other compounds of this type, could not be crystallised. Alcoholic soda simply removes methylic iodide, the original compound being formed again. It is probable that an intermediate leuco-base is formed, as at a certain stage in the action, a green dye is produced by the action of lead oxide and acetic acid, distinct from the violet dye produced under the same conditions from the original substance. It is noteworthy that the corresponding carbinol derivatives yield colouring matters with acetic acid alone, without the aid of oxidising agents.

The carbinol may conceivably act with methylic iodide in two ways, namely, as a tertiary amine or as a carbinol, and it is probable that the action proceeds in both directions, as a considerable quantity of a violet colouring matter, $CI(C_6H_4{\cdot}NMe_2)_3$, is formed, involving the production of an equivalent amount of the compound

$$OMe{\cdot}C(C_6H_4{\cdot}NMe_3I)_3.$$

The main product of the action of methylic iodide is, however, the simple additive product $OH{\cdot}C(C_6H_4{\cdot}NMe_3I)_3,3H_2O$. This may be partially dehydrated by heating in methylic iodide vapour at 150°, but under ordinary conditions it loses methylic iodide before the water of hydration is expelled. *Hexamethyltriamidotriphenylcarbinol trimethiodide* forms colourless crystals, and is much more soluble in water than the corresponding hydrocarbon derivative. It is partially converted by caustic alkalis, and completely by moist silver oxide, into the corresponding *hydroxide*, $OH{\cdot}C(C_6H_4{\cdot}NMe_3{\cdot}OH)_3$, which forms a transparent, non-crystalline, almost colourless mass, having a strong alkaline reaction. Its reactions are similar to those of the tetralkylammonium hydroxides.

*Methoxyhexamethyltriamidotriphenylmethane*, $OMe{\cdot}C(C_6H_4{\cdot}NMe_2)_3$, is formed by the action of caustic soda on a methyl alcoholic solution of the corresponding hydrochloride, "crystal violet"; it is an iridescent, crystalline powder melting and decomposing at 165°. The corresponding *ethoxy-compound* melts at 143°. The *amyloxy-compound* was also prepared. The *trimethiodide* of the methoxy-compound, with $3H_2O$, is formed with development of heat, by the direct addition of methylic iodide to the methylic derivative of the carbinol. It is a colourless substance which may be partially dehydrated in methylic iodide vapour at 150°. The corresponding derivative of the ethoxy-compound crystallises in large, anhydrous prisms, which are heavy and opaque. The *amyloxy*-compound is pulverulent, and very freely soluble in water.

The green dyes obtained from the products intermediate between the trimethiodides and the dimethylamido-compounds, by oxidising them with lead oxide and acetic acid, could not be purified, but their identity was established by synthesis. The *methiodide* of the methoxy-compound, $NMe_3I{\cdot}C_6H_4{\cdot}C(OMe)(C_6H_4{\cdot}NMe_2)_2$, the principal product of the direct addition of methylic iodide, crystallises from methylic alcohol in colourless needles, and melts and decomposes at 195°. It is converted by acids into the corresponding *iodide*,

$$NMe_3I{\cdot}C_6H_4{\cdot}CI(C_6H_4{\cdot}NMe_2)_2,$$

a green dye crystallising in large needles, having a metallic lustre. When heated, this loses methylic iodide, and is converted into the original violet dye, but is converted by moist silver oxide into the corresponding *dihydroxy*-compound, a yellowish alkaline substance. The intermediate compound, $NMe_3I{\cdot}C_6H_4{\cdot}C(OH)(C_6H_4{\cdot}NMe_2)_2$, is similar. JN. W.

**Santonic acid and its Derivatives.** By LUIGI FRANCESCONI (*Gazzetta*, 1895, **25**, ii, 461—478; compare Abstr., 1894, i, 204).—*Monacetylsantonic acid*, $C_{15}H_{19}O_4Ac$, is obtained by boiling santonic acid with acetic anhydride, treating with sodium carbonate, and extracting the solution with ether; it crystallises in long needles melting at 197—198°, is soluble in alcohol or acetic anhydride, and is not hydrolysed by boiling water, but dissolves in alcoholic potash yielding a solution from which hydrochloric acid precipitates santonic acid.

*Diacetylsantonic acid*, $C_{15}H_{18}O_4Ac_2$, is prepared by boiling santonic acid with acetic anhydride and sodium acetate, the product being treated with sodium carbonate and extracted with ether; it crystallises in transparent needles, melts at 207°, and is soluble in alcohol and acetic anhydride. Although not hydrolysed by boiling water, it is by alcoholic potash, and from the solution hydrochloric acid precipitates metasantonic acid. Neither of these acetyl derivatives reacts with hydroxylamine.

Metasantonin (isosantonin), obtained by Valente's process (*Real. Accad. Lincei*, [3], **3**, 242) of heating santonic acid with sulphuric acid, melts at 137—138°, and dissolves readily in fuming hydrochloric acid, forming a compound with it from which metasantonin is again obtained on treatment with water. When boiled with hydroxylamine and calcium carbonate, it yields *metasantoninoxime*,

$$C_{15}H_{18}O_2{:}NOH,$$

which crystallises in long needles melting at 220°, and in a 1·6776 per cent. alcoholic solution has the specific rotation at 25° of $[\alpha]_D = -377°$; it is readily decomposed on boiling with dilute hydrochloric acid, yielding metasantonin. The oxime is easily reduced by zinc dust and hydrochloric acid with formation of *hydrometasantonin*, $C_{15}H_{20}O_3$, which crystallises from alcohol or acetic acid in brilliant needles melting at 181—182°, and may also be prepared by reducing metasantonin with zinc dust and hydrochloric acid; it does not react with acetic chloride, or with acetic anhydride and sodium acetate, and in a 2·8916 per cent. chloroform solution at 25° it has the specific rotation $[\alpha]_D = -102·6°$. *Hydrometasantoninoxime*, $C_{15}H_{20}O_2{:}NOH$, crystallises in small opaque needles, which turn brown at 190° and melt at 196°; in a 1·7924 per cent. alcoholic solution it has the specific rotation $[\alpha]_D = -239°$.

Metasantonic acid is best prepared by heating santonic acid dissolved in acetic acid in a closed tube at 300° for 7—8 hours. Methylic metasantonate, when heated with hydroxylamine hydrochloride and calcium carbonate, yields the corresponding *oxime*, $C_{16}H_{22}O_3{:}NOH$; this crystallises in large tablets melting at 171°, is readily hydrolysed by cold hydrochloric acid, and in a 2·9712 per cent. alcoholic solution at 25° has the specific rotation $[\alpha]_D = -175°$. The *oxime* of ethylic metasantonate obtained in the same way, resembles the methylic compound, and melts at 166°, but the oxime of metasantonic acid can only be obtained crystalline with difficulty.

*Acetylmetasantonic acid*, $C_{17}H_{22}O_5$, is prepared by boiling a solution of metasantonic acid in acetic anhydride; it is a white crystalline substance melting at 202—203°, is not hydrolysed by boiling water, and yields metasantonic acid with alcoholic potash. Ethylic metasantonate remains unaltered when boiled with acetic anhydride.

The author gives an improved process for preparing santonide; when dissolved in fuming hydrochloric acid, it is converted into *isosantonic acid*, $C_{15}H_{20}O_4$, which forms transparent crystals melting at 152°, and in a 3·3828 per cent. chloroform solution at 25° has the specific rotation $[\alpha]_D = -73·92°$. Its *barium*, *silver*, *copper*, and *lead* salts are sparingly soluble or insoluble in water. The *methylic* salt, $C_{15}H_{19}MeO_4$, separates from ether in large, porcelain-like crystals melting at 69—70°, and is very soluble in ether, alcohol, or ethylic acetate; it is not acted on by acetic anhydride, and in a 2·2916 per cent. chloroform solution at 27° it has the specific rotation $[\alpha]_D = -50·2°$. The *ethylic* salt melts at 76°, and is similar in appearance and properties. Isosantonic acid does not yield an acetyl derivative with acetic anhydride, but is converted into its anhydride, santonide; neither the acid nor its alkylic salts combine with hydroxylamine.

W. J. P.

**Thio-derivatives of Phenols.** By ARNOLD VOSWINKEL (*Chem. Centr.*, 1895, i, 1060; from *Pharm. Zeit.*, 1895, **40**, 241—242; compare Tassinari, Abstr., 1891, 186).—The product of the action of thionyl chloride on β-naphthol was dissolved in potash, and then treated with hydrochloric acid, when the original product, β-thionaphthol, separated out. It therefore follows that this compound is β-thionaphthol, and not β-naphthol sulphite, which would, under the given treatment, yield β-naphthol and potassium sulphite. The following thiophenols have been prepared. Thiophenol, m. p. 148° (Tassinari gives 150°), *thio-α-naphthol*, thio-orthocresol, and thioparacresol; *methylic thiosalicylate*, *thioguaiacol*, *thioeugenol*, which are liquids; *thioresorcinol*, m. p. 120°, *thiothymol*, m. p. 146°, *thiomenthol*, m. p. 52°. J. J. S.

**Hæmatoxylin and Brazilin. III.** By JOSEF HERZIG (*Monatsh.*, **16**, 906—918; compare Abstr., 1893, i, 426; 1894, i, 341).—When acetyltrimethylhæmatoxylin is warmed on the water bath with one-half its weight of chromic acid in glacial acetic acid solution, an *acetyl* compound is produced, which, after hydrolysis, is completely soluble in alkalis. After dissolving it in the latter, and reprecipitating by carbonic anhydride, it may be separated by means of alcohol into two portions; the crystalline portion, which is but sparingly soluble in alcohol, decomposes on exposure to the air, and on analysis gives numbers agreeing with the formula of *tetramethyldehydrohæmatoxylin*, $C_{16}H_{15}O(OMe)_4{\cdot}OH$. It melts at 202—206°.

*Pentamethyldehydrohæmatoxylin*, $C_{10}H_5O(OMe)_5$, is formed on treating the preceding compound with alkali and methylic iodide. It is quite stable, and may readily be obtained in a pure state; it is only very sparingly soluble in alcohol, separating from the solution in beautiful white needles, which melt at 160—163°. It appears to react with bromine.

Tetramethyldehydrohæmatoxylin, when heated with acetic anhydride and sodium acetate, yields an *acetyl* derivative,

$$C_{10}H_5O(OMe)_4{\cdot}OAc,$$

which is slightly soluble in alcohol, crystallises in white needles, and melts at 190—192°.

The above compounds contain four atoms of hydrogen less than the corresponding hæmatoxylin derivatives.

Hæmatoxylin, when fused with caustic potash, yields almost at once a black substance, insoluble in all media with the exception of alkalis; it is not affected when kept in fusion with potash at 300—350° during two days.

*Trimethyldehydrobrazilin*, $C_{10}H_5O(OMe)_3OH$, is formed by the oxidation of trimethylacetylbrazilin and hydrolysis of the resulting acetyl derivative; it is even more unstable than the hæmatoxylin derivative above mentioned, and was not obtained pure. On acetylation, it yields an *acetyl* derivative, $C_{16}H_5O(OMe)_3{\cdot}OAc$, which separates from alcohol, in which it is but slightly soluble, in white, shimmering leaflets, and melts at 174—176°.

*Tetramethyldehydrobrazilin*, $C_{16}H_5O(OMe)_4$, produced by the methylation of the corresponding trimethyl derivative, is sparingly soluble in all media, and has not been obtained with any constant melting point. The specimen analysed melted at 136—155°.

The oils obtained at the same time as tetramethyldehydrohæmatoxylin and trimethyldehydrobrazilin appear to contain isomerides of these substances, and, on methylation, yield crystalline compounds having the compositions of pentamethyldehydrohæmatoxylin and tetramethyldehydrobrazilin respectively. A. L.

**Russian Oil of Aniseed.** By GEORGES BOUCHARDAT and TARDY (*Compt. rend.*, 1896, **122**, 198—201).—Russian oil of aniseed consists mainly of anethoïl, but also contains small quantities of anisic camphor, anisaldehyde, which boils at 245—248°, sp. gr. = 1·141 at 0°, and a substance which has the composition $C_{10}H_{10}O_2$ or $C_{10}H_{12}O_2$, yields anisic and acetic acids on oxidation, and seems to be anisic ketone (b. p. about 263°, sp. gr. = 1·095 at 0°). Minute quantities of anisic acid are also present. C. H. B.

**Oil of Scotch Fir (Pinus sylvestris) and other Pine Oils.** By JOHN C. UMNEY (*Pharm. J. Trans.*, 1895, **55**, 161 and 542).—The oil of *Pinus sylvestris* may show differences of rotation, depending on the season of the year when the materials are gathered or on the conditions of climate and soil. These differences in rotation should not exceed 20° in either direction in a 100-mm. tube. The sp. gr. of the oil should not fall below 0·880 at 15°. A very considerable part of the oil should distil above 185°, and not more than 15 per cent. below 170°.

The oil of *Abies canadensis* showed a sp. gr. of 0·9026 at 15°, and a rotation of −25° in a 100-mm. tube. This oil contained about 29·4 per cent. of bornylic acetate, and gave no indication of sylvestrene by Wallach's reaction.

The oil of *Abies excelsa* is that commonly sold as pine-needle oil, but it is easily distinguished by its lower specific gravity and its marked lævorotation of −70°. Oil of *Picea vulgaris* had a sp. gr. = 0·8806 at 15°, and a rotation of −37° in a 100-mm. tube. Oil of *Pinus pumilio* had a sp. gr. = 0·865—0·870, and a rotation of −7·5°. R. R.

**Oxidation of Pinene.** By GEORG WAGNER and GEORG ERTSCHIKOWSKY (*Ber.*, 1896, **29**, 881—885; compare Abstr., 1894, i, 610).—*Pinononic acid*, $C_9H_{14}O_3$, obtained by oxidising French turpentine with a 1 per cent. solution of potassium permanganate at 0°, crystallises from chloroform in transparent rhombohedra and prisms; it dissolves sparingly in cold water, and is insoluble in petroleum. The acid melts at 128—129°, and the *oxime*, which crystallises from water in plates, melts at 178—180°; a second *acid*, arising from the oxidation of pinene, and resembling cotton wool when crystallised from water, melts at 103—104°, and does not combine with hydroxylamine. Pinononic acid is also formed when the keto-alcohol, $C_{10}H_{16}O_2$ (*loc. cit.*), remains in contact with silver oxide for several weeks; alkali hypobromite converts it into the *acid*, $C_8H_{12}O_4$, which crystallises in transparent prisms and melts at 173—174°; bromoform and carbon tetrabromide being produced at the same time.

Among the neutral products of oxidation of French turpentine is an aldehyde which, on exposure to air, yields an acid resembling the camphenylic acid (m. p. 171·5—172·5°) obtained from camphene.

The authors point out that the production of pinononic acid is fresh evidence in favour of Wagner's formula for pinene, already supported by von Baeyer (this vol., i, 245) on obtaining α-pinonic acid from the hydrocarbon. M. O. F.

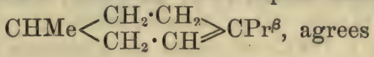
**Constitution of Pinene.** By GEORG WAGNER and ALEXANDER GINZBERG (*Ber.*, 1896, **29**, 886—890; compare foregoing abstract).—The statement of Wheeler relating to the behaviour of pinene towards hypochlorous acid has been confirmed, a compound, $C_{10}H_{17}O_2Cl$, being obtained in large, transparent, rhombic crystals; two modifications are produced, melting at 131—133° and 105—107° respectively, the former being more sparingly soluble in a mixture of ether and methylic alcohol. The compound is probably a monochlorhydrin of pinolglycol, the latter substance being produced along with it. Hypobromous acid converts pinene into Wallach's pinene bromide, which melts at 169—170° (Abstr., 1891, 1241).

The authors adhere to Wagner's formula for pinene.

M. O. F.

**The Pinene Problem.** By FERDINAND TIEMANN (*Ber.*, 1896, **29**, 890—892; compare the two foregoing abstracts).—A polemical paper, in which the author criticises Wagner's views, and advocates the formula for pinene put forward by Semmler and himself.

M. O. F.

**Constitution of Menthene and its Products of Oxidation.** By ST. TOLLOCZKO (*Chem. Centr.*, 1895, **1**, 543—544; from *Anz. Akad. Wiss., Krakau*, 1894, 267).—By the oxidation of menthene, $C_{10}H_{18}$, with potassium permanganate, the author has obtained *menthene glycol*, $C_{10}H_{18}(OH)_2$, in two physically isomeric forms, one of which is a liquid and the other a crystalline solid. A ketone-alcohol, $C_{10}H_{17}O\cdot OH$, which is a liquid, $[\alpha]_D = -1° 35'$, $K_{13\cdot5} = 104\cdot5—105\cdot5°$. and various acid products formed by the decomposition of the original menthene molecule were also obtained. The representation of menthene by the formula  $CHMe<{CH_2\cdot CH_2 \atop CH_2\cdot CH}\geqslant CPr^{\beta}$, agrees with these facts.

Menthol, when treated with sulphuric acid, yields a hydrocarbon, *menthane*, $C_{10}H_{20}$, having the properties of a polymethylene derivative. Other products are also formed; among these the author has found cymenesulphonic acid and a *hydrocarbon*, $C_{20}H_{36}$. J. J. S.

**Camphene Bromide.** By ALBERT REYCHLER (*Ber.*, 1896, **29**, 900—901; compare Jünger and Klages, this vol., i, 313).—When camphene is brominated in a mixture of ether and alcohol, and the product, after precipitation with water, submitted to distillation in an atmosphere of steam, an oil is obtained, which probably has the formula $C_{10}H_{15}Br$; *camphene bromide*, $C_{10}H_{16}Br_2$, which remains in the distilling flask, crystallises from alcohol in colourless, doubly refractive prisms, melting at 90°. The derivative is also formed when the bromination is conducted at −10°, light petroleum being employed as the medium. M. O. F.

**Geraniol and Rhodinol.** By JULIUS BERTRAM and EDUARD GILDEMEISTER (*J. pr. Chem.*, 1896, [2], **53**, 225—237; compare Abstr., 1894, i, 253).—The authors review the history of geraniol, and summarise the present knowledge of this alcohol as follows: (1) The alcoholic portion (b. p. about 230°) of Indian geranium oil (*Andropogon Schœnanthus*), of citronella oil (*Andropogon Nardus*), and of rose oil, consists exclusively or nearly so, of geraniol; the same is true of Barbier's licarhodol (Abstr., 1893, i, 544). (2) The essential oil of the pelargoniums (the French, African, and Reunion geranium oil) contains a considerable proportion of geraniol in that part of the alcoholic constituent which boils at 225—230°; but there is also present a second alcohol, which has not yet been obtained in a pure condition, and whose properties and composition have, in consequence, not been determined. This second alcohol appears, however, to be differentiated from geraniol by its lower boiling point, its lower specific gravity, and its behaviour towards hydrogen chloride and towards calcium chloride, with which it forms no solid compound. According to Barbier and Bouveault (Abstr., 1895, i, 4), the new alcohol yields α-methyladipic acid by energetic oxidation, whilst geraniol yields terebic acid.

The work of Erdmann and Huth (this vol., i, 198) is next unfavourably criticised; it is complained that these authors have obscured the issue by substituting the name rhodinol for geraniol.

Geraniol, prepared from the calcium chloride compound, was shaken with not quite anhydrous formic acid at the ordinary temperature, the product, after being saponified, was distilled, and the 175—185° fraction was shaken with chromic acid mixture (Baeyer, Abstr., 1894, i, 297); the oil which was then distilled over with steam no longer gave any reaction with chromic acid, and, when brominated, yielded dipentene tetrabromide, showing that dipentene, besides terpinene, is obtained by the action of formic acid on geraniol.

A. G. B.

**The Alleged Identity of Reuniol, Rhodinol, and Geraniol.** By ALBERT HESSE (*J. pr. Chem.*, 1896, [2], **53**, 238—241; compare Abstr., 1895, i, 186).—A reply to Erdmann and Huth (this vol., i, 198). The author maintains the individuality of reuniol, and points out that he has already prepared and patented many ethereal salts such as Erdmann and Huth claim to have discovered.

A. G. B.

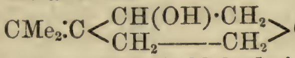
**Method of purifying Alcohols.** By FERDINAND TIEMANN and PAUL KRÜGER (*Ber.*, 1896, **29**, 901—903).—Many alcohols of the terpene series undergo change when submitted to the influence of acidic agents or the prolonged application of heat, and the authors accordingly employ a method of purifying alcohols which is independent of these conditions. In purifying linalol, for instance, sodium is dissolved in the alcohol, which is then distilled under reduced pressure from the sodium derivative; the latter is suspended in dry ether, and treated with succinic, or, preferably, phthalic anhydride, remaining in contact with it during several days. On agitating [the liquid with water, the linalolic sodium phthalate is dissolved, and after being repeatedly washed with ether, the solution is acidified and again extracted with that agent; the ethereal salt is then hydrolysed with alcoholic potash, and the pure alcohol is obtained from this liquid by precipitation with water. The yield amounts to 40—60 per cent. of the crude material.

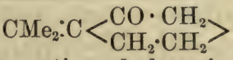
M. O. F.

**Compounds of the Citronellal Series.** By FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1896, **29**, 903—926; compare Abstr., 1891, 285 and 539; 1892, 1068; also 1895, i, 646).—Citronellaldehyde, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}COH$ (compare Abstr., 1893, i, 685), boils at 205—208° under atmospheric pressure, and at 103—105° under a pressure of 25 mm.; the specific rotatory power $[\alpha]_D = +12·5°$, the sp. gr. = 0·8538 at 17·5°, the refractive index $n_D = 1·4481$, and the molecular refraction M = 48·29.

Citronellol, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH$, was obtained by Dodge on reducing citronellaldehyde with sodium amalgam and glacial acetic acid; it boils at 117—118° under a pressure of 17 mm., has the specific rotatory power $[\alpha]_D = +4°$ at 17·5°, the sp. gr. = 0·8565 at 17·5°, the refractive index $n_D = 1·45659$, and the molecular refraction M = 49·57. The *acetate* boils at 119—121° under a pressure of 15 mm., has the specific rotatory power $[\alpha]_D = +2·37°$ at 17·5°, and the sp. gr. = 0·8928 at 17·5°; the refractive index $n_D = 1·4456$ at 17·5°, and the molecular refraction M = 59·56. The *formate* boils at 97—100° under a pressure of 10 mm. When citronellol is agitated with 10 per cent. sulphuric acid, a viscous, colourless oil is obtained, boiling at 144—146° under a pressure of 10 mm.; dehydrating agents regenerate citronellol from the substance, which is probably a dihydric alcohol arising from the addition of $1H_2O$ to the alcohol.

Oxidation with potassium permanganate, followed by chromic and sulphuric acids, convert citronellaldehyde, citronellol, and citronellic acid into dextro-β-methyladipic acid, which melts at 84—85° (compare Semmler, *loc. cit.*); previous investigators have obtained this substance from menthol, pulegone, menthone, and dimethyl-2 : 6-octane ol-3-oic acid (this vol., i, 247), and the question of its constitution is discussed by the authors.

*Isopulegol*,  $CMe_2{:}C{<}\begin{matrix}CH(OH)\cdot CH_2\\ CH_2\text{———}CH_2\end{matrix}{>}CHMe$, is obtained in the form of the acetate when citronellaldehyde is heated with an equal weight of acetic anhydride in autoclaves for 10—12 hours at 180—200°, or in presence of anhydrous sodium acetate for 15—20 hours at 150—160°; it has the odour of menthol, boils at 91° under a pressure of 13 mm., and has the specific rotatory power $[\alpha]_D = -2·65°$. The sp. gr. = 0·9154 at 17·5°, the refractive index $n_D = 1·47292$, and the molecular refraction M = 47·20.

*Isopulegone*,  $CMe_2{:}C{<}\begin{matrix}CO\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}CHMe$, is produced on oxidising isopulegol with acetic and chromic acids, and boils at 85—90° under a pressure of 13 mm., whilst pulegone from polei oil boils at 99—101° under a pressure of 14 mm.; both isomerides are, however, dextrorotatory. When isopulegone is treated with hydroxylamine, pulegoneoxime (m. p. 120—121°), which is volatile in an atmosphere of steam, is produced, as also an *oxime* which melts at 134° and is not volatile. The semicarbazone is identical with the compound from polei oil (Abstr., 1895, i, 380), and when this substance, or the oxime melting at 121° is treated with boiling dilute sulphuric acid and alcohol, it yields methyl-1-cyclohexanone-5 (Wallach, this vol., i, 309).

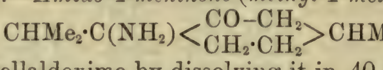
The authors enumerate several sources of citronellol, and state that the latter may be separated from admixture with geraniol by heating the liquid with phthalic anhydride at 200° for about two hours, geraniol being converted into the hydrocarbon by this treatment; the phthalic salt of citronellol is then washed and hydrolysed. When the proportion of citronellol in the liquid is small, a method is adopted in which phosphorus trichloride is employed, the alcohols being converted into their phosphates, and then separated.

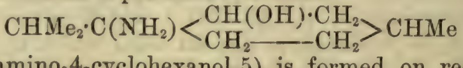
Turkish rose oil contains 80 per cent. of alcohols, boiling at 112—116° under a pressure of 12 mm.; these consist of geraniol and citronellol in the proportion of three to one. Citronellol obtained from this source has been hitherto called rhodinol, and is lævogyrate, having the rotation $\alpha = -4° 20'$ in a 1 decimeter tube; the sp. gr. $= 0{\cdot}8612$ at 20°, the refractive index $n_D = 1{\cdot}45789$, and the molecular refraction $M = 49{\cdot}43$. Oxidation on the lines indicated for *d*-citronellol converts rhodinol into lævo-$\beta$-methyladipic acid, which melts at 84·5°, and has the rotation $\alpha = -2°$ in 33 per cent. aqueous solution; when equal weights of *d*- and *l*-$\beta$-methyladipic acid are crystallised together, the racemic modification is produced, and crystallises in needles melting at 93—94°. Unlike the odours of bitter almond, vanilla, heliotrope, and violet oils, the perfume of rose oil does not depend on an individual constituent, but is due to several, and the artificial preparation of this scent can no longer be regarded as a purely chemical problem.

Spanish geranium oil contains 70 per cent. of mixed alcohols, consisting of 65 per cent. of geraniol and 35 per cent. of *d*- and *l*-citronellol, of which the latter preponderates; in African geranium oil, the alcohols amount to 75 per cent., of which 80 per cent. is geraniol, whilst 20 per cent. is a lævogyrate mixture of citronellols. Reunion geranium oil (pelargonium oil) contains 80 per cent. of alcohols consisting of 50 per cent. of geraniol.

The recent observation of Barbier and Bouveault, who obtained citronellol and menthone on carefully oxidising pelargonium oil (*Compt. rend.*, 1896, **122**, 737), has not been confirmed by the authors.

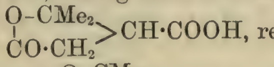
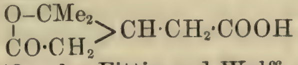
M. O. F.

**Two Oxygenated Bases from Citronellaldoxime.** By FERDINAND TIEMANN and PAUL KRÜGER (*Ber.*, 1896, **29**, 926—928; compare foregoing abstract).—*Amido*-4-*menthone* (*methyl*-1-*methoethyl*-4-*amino*-4-*cyclohexanone*-5),  $CHMe_2\cdot C(NH_2)<\begin{matrix}CO-CH_2\\CH_2\cdot CH_2\end{matrix}>CHMe$, obtained from the isomeric citronellaldoxime by dissolving it in 40 per cent. sulphuric acid, boils at 118° under a pressure of 13 mm.; the *acetyl* derivative boils at 142° under a pressure of 12 mm.

*Amido*-4-*menthol*,  $CHMe_2\cdot C(NH_2)<\begin{matrix}CH(OH)\cdot CH_2\\CH_2\text{———}CH_2\end{matrix}>CHMe$ (methyl-1-methoethyl-4-amino-4-cyclohexanol-5), is formed on reducing the foregoing base with glacial acetic acid and iron, and boils at 125° under a pressure of 12 mm.; it readily absorbs carbonic anhydride from the atmosphere, and the *acetate* crystallises from benzene in slender, white needles, melting at 137°.

The authors regard the production of the former base as analogous to the conversion of camphoroxime into isoamidocamphor.

M. O. F.

**Terpenylic acid.** By Friedrich Mahla and Ferdinand Tiemann (*Ber.*, 1896, **29**, 928—935).—The authors discuss the constitution of terpenylic acid, and, basing their deductions on the accepted formula for terebic acid,  $\begin{array}{l}\text{O-CMe}_2\\ \vert\\ \text{CO}\cdot\text{CH}_2\end{array}\!\!>\text{CH}\cdot\text{COOH}$, represent the former substance by the expression,  $\begin{array}{l}\text{O-CMe}_2\\ \vert\\ \text{CO}\cdot\text{CH}_2\end{array}\!\!>\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$ (compare Schryver, Trans., 1893, **63**, 1342; also Fittig and Wolff, this vol., i, 135).

The oxidation of terpenylic to terebic acid is described, and also the production of the latter from methoethyl-5-heptanon-2-olide-$5^1 : 7$, which may be used profitably as a source of terpenylic acid (compare Abstr., 1894, i, 44). M. O. F.

**Campholide, a Product of Reduction of Camphoric Anhydride.** By Albin Haller (*Compt. rend.*, 1896, **122**, 293—297).—When an alcoholic solution of camphoric anhydride is reduced by means of sodium amalgam, the liquid being kept acid by addition of sulphuric acid, a small quantity of *campholide*, $C_{10}H_{16}O_2$, is obtained. Aluminium amalgam gives a less satisfactory result.

Campholide forms white crystals, with an odour of camphor, has a hot, burning taste, and is only slightly soluble in water, but extremely soluble in most organic solvents, and its solutions are optically inactive. It melts at 211° (corr.), and sublimes readily. It forms salts with metals, and the copper salt is insoluble in alcohol and water. When oxidised with permanganate, the campholide yields camphoric acid, and when heated with potassium cyanide, it is converted into cyanocampholic acid, from which camphor can be obtained.

This campholide, although similar in composition, differs considerably in properties from the campholide described by M. O. Forster (Trans., 1896, 55). C. H. B.

**Convolvulus Resins.** By Nicolai Kromer (*Chem. Centr.*, 1895, ii, 228, 449—450, and 495; from *Zeit. Öster. Apoth. Verein*, 1895, **49**, 418—422, 437—443, 455—459, and 479—484).—Spirgatis has shown that scammonin, from *Convolvulus Scammoniæ* L., is identical with jalapin, from *C. orizabeus* Pell. Purified jalapin is obtained as a colourless, crystalline powder by dissolving the crude product in alcohol (96 per cent.) and allowing the solution to remain during several weeks at a low temperature; it melts at about 142°, the molecular weight = 2000—3000, $[\alpha]_D = -22{\cdot}84$ to $-23{\cdot}83°$, the value for scammonin $= -23{\cdot}06$. The mother liquor contains a compound, $C_{18}H_{30}O$, which crystallises in large, white plates.

By the action of alkali on the glucosides, acids and other substances are formed; lactone derivatives could not be isolated. Both jalapin and scammonin require about 22—23 per cent. of potash for their decomposition.

By the action of baryta water, various substances are formed, o which the portion not volatile with steam and insoluble in ether consists of *jalapic* or *scammonic acid*, $C_{45}H_{78}O_{27}$; it softens at

155—165°, melts at 208°, is feebly acid, and slowly decomposes carbonates; $[\alpha]_D = -29{\cdot}6°$ to $-28{\cdot}95°$. The *barium* salt has been analysed. The non-volatile product, soluble in ether, possibly consists of a *tetrahydroxydecoic acid*, $C_{10}H_{20}O_6$; the *barium* and *silver* salts are crystalline, the latter being deposited in needles; the *copper*, *zinc*, and *sodium* salts have also been prepared. The products of hydrolysis, volatile with steam, consist of methylethylacetic acid and tiglic acid, and, in traces, an acid, probably formic, which reduces silver, gold, and mercury salts.

By the action of dilute acids on the glucosides, a sugar, probably *d*-glucose, and *jalapinolic* or *scamminolic acid*, $C_{16}H_{30}O_3$ (?), are produced.

The preceding results show that jalapin and scammonin are identical, but, as the formula of jalapinolic acid is doubtful, none can be given for the glucoside. Turpethin, the active constituent of the root of *Ipomœa turpethum* (Abstr., 1893, i, 424), is identical with jalapin in percentage composition; when treated with baryta water, *turpethic acid* is formed, which is colourless and not volatile with steam. The behaviour of jalapic acid towards litmus and phenolphthaleïn suggests that it may be a phenol. J. B. T.

**Acokanthera Schimperi.** By THOMAS R. FRASER and JOSEPH TILLIE (*Pharm. J. Trans.*, 1895, **55**, 76).—The authors have been able to refer several specimens of wood, from which native tribes in East Africa prepare arrow poison, to the genus *Acokanthera.* They have extracted from the leaves, flowers, and fruit of *Acokanthera schimperi* the active principle as a crystalline glucoside, $C_{30}H_{48}O_{13}$, identical with that contained in the wood. It is very soluble in water, from which it crystallises in colourless, transparent, quadrangular plates. From alcohol, in which it is much less soluble, it separates in needle-shaped crystals. The aqueous solution is neutral in reaction and tasteless. Few chemical reagents affect it, but strong sulphuric acid produces at once a red colour, and this afterwards changes to green. With dilute sulphuric acid, it gives the reaction of a glucoside. The characters of this active principle agree with those of the glucosides that have been separated from the woods of several unidentified species of *Acokanthera*, and with that derived from a species of *Strophanthus* obtained from West Africa. R. R.

**Ricinin.** By MARCO SOAVE (*Chem. Centr.*, 1895, i, 853; from *Ann. Chim. Farm.*, **21**, 49—61).—*Ricinin*, $C_{17}H_{18}N_4O_4$, is the poisonous principle of the castor oil seeds. The pressed seeds yield 0·3 per cent., whereas the husks yield 1·5 per cent. of ricinin. To obtain the ricinin, the pressed seeds or husks are extracted with boiling water, the extract evaporated on the water bath, and the residue treated with alcohol. The alcoholic solution is then evaporated to dryness and the residue treated with caustic soda; by this means, the impurities are dissolved out, and the ricinin which remains behind may be crystallised from alcohol or water. It crystallises in glistening plates, melts at 194°, has a bitter taste, is readily soluble in water, alcohol, chloroform, benzene, and ether; the aqueous solution is neutral and optically inactive. Ricinin may be sublimed when carefully heated; it is soluble in concentrated sulphuric acid, yielding a colourless solution, which becomes straw-yellow, and then bright claret red, on warming. The colourless sulphuric acid solution gives, with a crystal of potassium dichromate, a bright green coloration; the author suggests this as a test for ricinin. Ricinin does not give the usual tests for alkaloïds, neither does it form salts with strong mineral acids; it yields a *bromo*-derivative, $C_{17}H_{16}Br_2N_4O_4$, which melts at 247°, and a corresponding *chloro*-derivative, which melts at 240°. With mercuric chloride, it yields the *compound*, $C_{17}H_{13}N_4O_4,2HgCl_2$, which melts at 204°. When oxidised, it yields a new acid, $C_{15}H_{14}N_4O_4$, which the author terms *ricininic acid;* the same acid may also be obtained by the hydrolysis of ricinin with caustic soda. It is a dibasic acid, which melts at 295°, yields a *silver* salt, a *barium* salt crystallising with $4H_2O$, and a *bromo*-derivative, $C_{15}H_{12}Br_2N_4O_4$, melting at 180°. J. J. S.

**Polystichic acids.** By C. Poulsson (*Chem. Centr.*, 1895, i, 887; from *Arch. Exp. Path. Pharm.*, 1894, **35**, 97—104).—The author has obtained two new acids from the rhizomes of *Polystichum spinulosum*, taken in the autumn. One of these is *polystichic acid*, $C_{22}H_{24}O_9$, which melts at 123—123·2°; it is insoluble in water, readily soluble in chloroform, ether, and benzene, and crystallises in yellowish needles. The second acid is *dihydropolystichic acid*, $C_{22}H_{26}O_9$, which crystallises in white, granular masses or colourless needles, and melts at 150°. The two acids are best separated by crystallisation from acetone and then by treatment with chloroform and methylic alcohol. Both are poisonous, and resemble filicic acid in their physiological action. The fatal dose for frogs is 2 milligrams, for rabbits 0·03—0·05 gram per kilo. of body weight. J. J. S.

**Turmerole.** By C. Loring Jackson and William H. Warren (*Amer. Chem. J.*, 1896, **18**, 111—117).—Turmerole, a compound obtained from the oily extract of turmeric (Abstr., 1883, 482), was purified by fractional distillation under reduced pressure. It is a yellowish oil, with a peculiar, agreeable odour, and its sp. gr. = 0·9561 at 24°/4°. It mixes easily with the common solvents, but is insoluble in water. It is partially decomposed by distillation under the ordinary pressure, but distils unchanged between 158° and 163° at 11—12 mm. pressure. Analyses of different fractions agreed in indicating the formula $C_{13}H_{18}O$, or possibly $C_{14}H_{20}O$. Dilute nitric acid converted turmerole into paratoluic acid. Turmerole therefore contains a benzene ring with a methyl group, and a side-chain of six or seven carbon atoms in the positions 1 : 4. The side-chain contains an asymmetric carbon atom, the specific rotation of turmerole being $[\alpha]_D = 24·58°$. A. E.

**Chemistry of Red Vegetable Colouring Matters.** By Leopold Weigert (*Bied. Centr.*, 1896, **25**, 58—59; from *Jahresber. k. k. Wein u. Obstbaulehranst. Klosterneuburg*, 1894–95).—There are two groups of red dyes (1) wine-red, including the colouring matter of grapes, reddened vine leaves, leaves of the wild vine, *Rhus typhina*, *Cornus sanguinea*,

&c. They give the following reactions: lead acetate, bluish-green or grey precipitates; cold concentrated hydrochloric acid, brighter red coloration and precipitation; ammonia, alkalis or alkaline earths, greenish colour. Group (2) includes the red dyes of beet-root, the leaves of iresine, amaranth, and achyrantes, and the fruit of *Phytolacca decandra*. With lead acetate, these dyes yield red precipitates, but do not give Erdmann's reaction, and are changed to dark violet by strong, cold hydrochloric acid. In slightly alkaline solutions, they retain their red colour, but excess of ammonia gives a dark violet, and excess of alkalis and alkaline earths first violet-brown, then a bright yellow coloration. The red dye is not extracted from the dried plants by alcohol, but dissolves in water.

Wine-red is nearly related to the violet or dark red dyes of *Coleus Verschaffelti*, *Perilla nankinensis*, *Ajuga reptans*, *Prunus Pissardi*, and the bluish-skinned potato cabbage, the blue bean, and the mallow.

Blue grapes and bilberries contain a red-brown dye, insoluble in acidified water, and a soluble dye, which, when boiled with acid, yields sugar and the insoluble dye. The deposition of the colouring matter of red wine is due to the conversion of the soluble into the insoluble dye. There seems to be no direct connection between these dyes and chlorophyll, but they protect chlorophyll from the action of light. Red autumn leaves show much less evaporation than green leaves.

N. H. J. M.

**Mercuropyridine Compounds.** By LEONE PESCI (*Gazzetta*, 1895, **25**, ii, 423—433; compare this vol., i, 186).—*Pyridine mercuro- (mercuropyridine) chloride*, $(C_5NH_5)_2HgCl_2$, formed with development of heat on treating mercuric chloride with pyridine, crystallises from pyridine in colourless, lustrous needles melting at 108°. It is decomposed on boiling with alcohol or water, yielding Lang's salt, $(C_5NH_5)_2HgCl_2,HgCl_2$ (*Ber.*, 1888, 1586), which crystallises in colourless needles melting at 120—180°. Monari's salt,

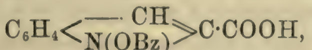
$$(C_5NH_5)_2HgCl_2,2HgCl_2$$

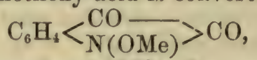
crystallises in lustrous, colourless needles melting at 194—195°. *Pyridine mercuric hydroxide*, $(C_5NH_5)_2Hg(OH)_2$, can only be obtained in aqueous solution by treating the corresponding chloride with silver hydroxide or by the prolonged boiling of yellow mercuric oxide with aqueous pyridine solution. It is most conveniently prepared by adding excess of barium carbonate to pyridine mercuric sulphate solution; the filtrate from the carbonate and sulphate deposits basic mercuric carbonate, $3HgO,CO_2$, in lustrous red needles. The solution of the hydroxide is colourless and strongly alkaline, and has the odour and taste of aqueous pyridine solution; it deposits yellow mercuric oxide on evaporation, and, when evaporated with nitric acid, deposits *pyridine mercuric nitrate*, $(C_5NH_5)_2Hg(NO_3)_2,2H_2O$, which crystallises in colourless needles, and effloresces in a dry atmosphere. The corresponding *sulphate*, $(C_5NH_5)_2HgSO_4,4H_2O$, is prepared by adding mercuric sulphate and a little yellow mercuric oxide to pyridine solution; it crystallises in large, monoclinic prisms which are very soluble in water, and lose $2H_2O$ in dry air. W. J. P.

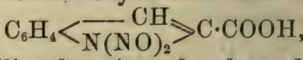
**2 : 6-Diphenylpyridine and Piperidine.** By CARL PAAL (*Ber.*, 1896, **29**, 798—800).—2 : 6-Diphenylpyridine was prepared by Scholtz from cinnamylideneacetophenone oxime (Abstr., 1895, i, 562), by Paal and Strasser from diphenacylmalonic acid, and by Doebner and Kuntze from α-phenylnaphthocinchonic acid; although the bases are identical, the platinochlorides described by Scholtz and by Paal differ in melting point and solubility; they have, therefore, been reinvestigated, and are found to be identical, the differences being due to impurity in Paal and Strasser's preparation. The compound melts at 195°, and is sparingly soluble. 2 : 6-Diphenylpiperidine was previously described as an oil both by Paal and Strasser, and by Scholtz. If prepared from purified diphenylpyridine, it crystallises from alcohol, on the addition of water, in large, colourless, transparent plates melting at 69°. The hydrochloride melts at 298°, but, after treating it with ether, regenerating the base, and reconverting it into the hydrochloride, the latter melts at 315—316°. The impurity in the diphenylpiperidine appears to have been derived from the common quicklime employed for the decomposition of the diphenyldipiperidinedicarboxylic acid. J. B. T.

**Reactions of Ethylic Orthonitrobenzylmalonate. I. Alkaline Hydrolysis; Synthesis of new Indole Derivatives.** By ARNOLD REISSERT (*Ber.*, 1896, **29**, 639—665; compare this vol., i, 392).—When ethylic orthonitrobenzylmalonate is heated with 33 per cent. aqueous soda, the normal reaction occurs, and *orthonitrobenzylmalonic acid*, $NO_2\cdot C_6H_4\cdot CH_2\cdot C(COOH)_2$, is formed; it crystallises in colourless, rectangular prisms, which melt and evolve gas at 161°. The *hydrogen ammonium salt*, obtained by adding hydrochloric acid to the normal salt, crystallises in prisms melting at 169°; the *normal salt* is more readily soluble in water, and melts at 172°. The *silver salt* is an amorphous, white precipitate.

When ethylic orthonitrobenzylmalonate is heated with an excess of alkali or boiled with alkali for some time, or when orthonitrobenzylmalonic acid is boiled with aqueous soda, 1′-*hydroxyindole*-2′-*carboxylic acid* is formed; it crystallises in stellate groups of small, white prisms which melt at 159·5°. The acid reduces Fehling's solution when heated, gives a cherry-red coloration with nitric acid, and dissolves in sulphuric acid, forming a colourless solution which becomes blue on heating. The alkaline solutions of the acid gradually become indigo coloured when kept; with bleaching powder, the aqueous solution of the acid gives a blue precipitate resembling indigo, whilst chromic acid produces a red precipitate. The salts are unstable, and not characteristic. The *methylic salt*, $C_8H_6NO\cdot COOMe$, crystallises in long, snow-white, lustrous needles, and melts at 100—101°. The *ethylic salt* crystallises in colourless, pointed prisms melting at 65°.

The 1′-*benzoyl-derivative*,  $C_6H_4<{}^{\overline{\quad CH}}_{N(OBz)}>C\cdot COOH$, forms snow-white, small crystals melting and decomposing at 151°. Acetic anhydride in the cold produces two compounds. The *mixed anhydride* *of acetic and hydroxyindolecarboxylic acids*, $C_{13}H_{11}NO_5$, forms colourless, lustrous needles which melt at 107°, and is decomposed by boiling water. 1′-*Acetoxyindole*-2′-*carboxylic acid* forms small, white needles, and melts at 161°. It dissolves without change in sodium hydrogen carbonate solution, but is at once hydrolysed by aqueous soda. 1′-*Methoxyindole*-2′-*carboxylic acid* is obtained by the action of sodium ethoxide and methylic iodide on the acid; it crystallises in lustrous, well-developed needles, and melts and decomposes at 185°. This acid is very stable, and is not acted on by Fehling's solution, ferric chloride, sodium nitrite, or hydrogen peroxide. The *silver salt* is soluble in a large amount of hot water. *Methylic* 1′-*methoxyindole*-2′-*carboxylate* is obtained by the action of methylic alcohol and hydrogen chloride on the acid just described, and by the action of sodium methoxide and methylic iodide on methylic hydroxyindolecarboxylate. It forms short, thick, rhomboid crystals, and melts at 68°. 1′-*Methoxyindole*-2′-*carboxylic chloride* crystallises in long, white needles melting at 61°. The *amide* crystallises in plates which resemble those of benzoic acid, and melt at 108°. Bromine converts the amide into a derivative which melts at 175°. 3′ : 1′-*Bromomethoxyindole*-2′-*carboxylic acid*, $C_{10}H_8NO_3Br$, crystallises in short, lustrous needles, and melts at 189°. Hydroxyindolecarboxylic acid is converted by reduction by means of zinc dust and acetic acid into the well-known $\alpha$-indolecarboxylic acid melting at about 203°. The same acid is formed when the methoxy-acid is reduced with sodium amalgam.

Potassium permanganate converts hydroxyindolecarboxylic acid into the orthazoxybenzoic acid which was first described by Griess *Ber.*, 1874, **7**, 1611). Chromic acid, on the other hand, converts the acid into isatin. The methoxy-acid is converted by this reagent into 1′-*methoxypseudoisatin*,  $C_6H_4<\genfrac{}{}{0pt}{}{CO\text{——}}{N(OMe)}>CO$, which forms small, brick-red needles, and melts at 110°. It resembles isatin in appearance, and gives, with sulphuric acid and thiophen, a reaction which closely resembles the indophenine reaction. It reduces Fehling's solution when warmed, and dissolves in alkalis. The *phenylhydrazone* melts at 128—129°. When reduced, methoxypseudoisatin appears to be converted into dioxindole. *Indoxin*, $C_{18}H_{12}N_2O_4$, is formed when hydroxyindolecarboxylic acid is treated with hydrogen peroxide, or when the mixed anhydride of acetic and hydroxyindolecarboxylic acids is treated with aqueous soda. It is a blue, crystalline substance which melts at 223°, and resembles indigo-blue very closely in appearance. It is soluble in hot water, the solution being decolorised by the addition of hydrochloric acid; it also dissolves in solutions of caustic alkalis, but not of their carbonates.

Nitrous acid converts the hydroxyindolecarboxylic acid into a nitramine, 1′-*nitroindole*-2′-*carboxylic acid*,  $C_6H_4<\genfrac{}{}{0pt}{}{\text{——}CH}{N(NO)_2}>C\cdot COOH$, which forms a lemon-yellow, micro-crystalline deposit, and melts and decomposes at 189°. It does not give Liebermann's reaction, neither does it form a benzoyl derivative. When methylic hydroxyindolecarboxylate is treated with nitrous acid, it forms an unstable, crystalline substance melting at 224—225°, the constitution of which has not been determined; if this is dissolved in dilute alkali and the solution acidified, the nitramine described above is precipitated. The substance melting at 224—225° is converted by boiling with ammonium sulphide into a crystalline base, which melts at 136°, and is probably *methylic* 1'-*amidoindole*-2'-*carboxylate.* The compound melting at 224—225° is accompanied by another substance which appears to have the composition $C_{10}H_9NO_3$, but has not yet been obtained pure.

A. H.

**Improvement of Skraup's Quinoline Synthesis.** By CHR. A. KNUEPPEL (*Ber.*, 1896, **29**, 703—709).—As is well known, the usual method of preparing a quinoline derivative is to heat the corresponding aromatic amido-derivative with glycerol in the presence of strong sulphuric acid and nitrobenzene. The last substance acts as an oxidising agent, but a much better yield is obtained if it is replaced by arsenic acid; only in the case of quinoline itself, in which case the nitrobenzene also takes part in the synthesis, was a larger yield obtained by the old method. To take an example, β-naphthaquinoline was prepared by heating together 100 grams of arsenic acid, 200 grams of concentrated sulphuric acid, 215 grams of glycerol, and 100 grams of commercial β-naphthylamine in the oil bath until the action began; when this had moderated, the flask was replaced in the bath, and the contents gently boiled for 3—4 hours. The mixture was then diluted with water, allowed to settle for some time, filtered, and the filtrate made alkaline with sodium hydroxide, when the naphthaquinoline separated as an oil that soon solidified. It was purified by boiling it in alcoholic solution with animal charcoal, and adding water to the filtered solution; the yield was 92—93 grams, melting at 93·5°. In a similar way there were prepared quinoline itself, and 1-methylquinoline, 1-nitroquinoline, 3-nitroquinoline, 3-dimethylamidoquinoline, 2-nitroquinoline, 2-dimethylamidoquinoline, β-anthraquinoline, dihydroxy-β-anthraquinoline (alizarin blue), and quinoline-3-sulphonic acid.

C. F. B.

**1 : 4-, 1 : 3-, and 2 : 4-Dinitroquinoline.** By ADOLPH CLAUS and GABRIEL HARTMANN (*J. pr. Chem.*, 1896, [2], **53**, 198—210).—1 : 4-*Dinitroquinoline* has been previously described as α-dinitroquinoline (Abstr., 1885, 908); conversion into 1 : 4-dibromoquinoline through the diazo-reaction has settled its orientation. The *hydrobromide* forms yellow crystals, melts at 230°, and readily combines with bromine to form a dibromide, which is convertible, in the usual manner (Claus-Collischon's method), into a 3'-*bromo*-1 : 4-*dinitroquinoline.* This crystallises in colourless needles, and melts at 152°.

4 : 1-*Nitramidoquinoline* was prepared by reducing the dinitroquinoline with ammonium sulphide; it forms columnar crystals, melts at 184°, and is a feeble base; replacement of the amido-group by a bromine atom gave a bromonitroquinoline, which has been already orientated; the *methiodide* is described; the *platinochloride* melts and decomposes at 246°. 4 : 1-*Nitracetamidoquinoline* sublimes in the

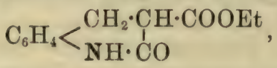
form of transparent, yellow needles, melts at 220°, and is sparingly soluble in hot water and hot alcohol.

1 : 3-*Dinitroquinoline* (β-dinitroquinoline, *loc. cit.*) melts at 144°, not 133—134° (*loc. cit.*); by bromination it yields a 3′-*bromo*-1 : 3-*dinitroquinoline*, which crystallises in colourless needles, melts at 120°, and dissolves in alcohol sparingly, and in water not at all.

3 : 1-*Nitramidoquinoline* crystallises in lustrous, red needles or columns, melts at 194°, and is sparingly soluble in hot water, but more freely in hot alcohol; the *methiodide* crystallises in red, lustrous needles, melts at 176°, and dissolves easily in hot alcohol, but only sparingly in cold water; the *platinochloride* is described. The easy formation of a methiodide seems to characterise amido-compounds in which the amido-group is in the 1-position. 3 : 1-*Nitracetamidoquinoline* sublimes in lustrous, yellow needles, melts at 224°, and is not very soluble either in water or alcohol.

2 : 4-*Dinitroquinoline* sublimes in the form of yellow, lustrous needles, melts at 179°, and is freely soluble in alcohol, ether, and chloroform, but not in water; the *hydrochloride* forms colourless crystals, and melts at about 86°; the *platinochloride* was prepared. By bromination, the dinitroquinoline yields a 3′-*bromo*-2 : 4-*dinitroquinoline*, which crystallises in colourless needles, melts at 161°, and sublimes unchanged.
A. G. B.

**Reactions of Ethylic Orthonitrobenzylmalonate. II. Reduction: Formation of Quinoline Derivatives.** By ARNOLD REISSERT (*Ber.*, 1896, **29**, 665—667).—When ethylic orthonitrobenzylmalonate is dissolved in alcoholic hydrogen chloride and treated with zinc dust, it is converted into *ethylic hydrocarbostyril*-3′-*carboxylate*,



$$C_6H_4<\begin{array}{l}CH_2\cdot CH\cdot COOEt\\ NH\cdot \overset{|}{C}O\end{array},$$

which crystallises in matted needles, melting at 137—138°. The free *acid* crystallises in short, thick prisms, and melts with evolution of carbonic anhydride at 146°, being thereby converted into hydrocarbostyril. The acid is readily soluble in acetic acid, alcohol, and hot water. The *silver salt* is soluble in hot water.
A. H.

**New Bromo-derivatives of Carbazole.** By GIROLAMO MAZZARA and ARISTIDE LEONARDI (*Gazzetta*, 1895, **25**, ii, 395—400; compare this vol., i, 304).—An improved method of preparing benzoyldibromocarbazole is described. No products of interest are obtained by the action of nitric acid on dibromocarbazole; its benzoyl derivative, however, when heated with nitric acid (sp. gr. 1·46) yields the bromodinitrocarbazole, melting at 255°.

Diamidocarbazole is formed on reducing dinitrocarbazole with tin and hydrochloric acid, but no nitramidocarbazole could be obtained. On nitrating the nitramidocarbazole melting at 213—214° in acetic acid solution, a *nitracetamidocarbazole*, which crystallises in minute yellow needles, is obtained, and, on hydrolysis with potash, yields a *nitramidocarbazole*; the latter is a crystalline, red powder, which does not melt, and of which the amidogen cannot be replaced by bromine.

*Acetyldibromocarbazole* is obtained from dibromocarbazole in the usual way, and crystallises in white needles, melting at 189—190° (corr.); on nitration, it yields bromine, polynitro-derivatives, and the bromodinitrocarbazole melting at 255°.

*Benzoyltribromocarbazole* is obtained, together with the dibromo-compound, on heating a carbon bisulphide solution of benzoylcarbazole with bromine; it crystallises in transparent, yellow laminæ or needles, melting at 228—230°, and is not attacked by boiling alcoholic potash.

*Pentabromocarbazole*, $C_{12}H_4NBr_5$, is prepared by boiling a chloroform solution of carbazole with bromine and a little iodine; it crystallises in minute, white needles melting at 273—274°, and is not acted on by acetic anhydride at 240°.

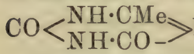
*Heptabromocarbazole* may be prepared by heating dibromocarbazole with bromine at 100° in a closed tube; it crystallises in whitish needles, which do not melt at 330°. W. J. P.

**Cyanalkines; Cyanobenzyline [4-Amido-5-phenyl-2 : 6-dibenzylmetadiazine].** By G. Herfeldt (*J. pr. Chem.*, 1896, [2], **53**, 246—250; compare Abstr., 1889, 684).—Cyanobenzyline (4-amido-5-phenyl-2 : 6-dibenzylmetadiazine) is best prepared by mixing dry sodium ethoxide with benzylic cyanide to a stiff paste, and heating the mixture in an autoclave for 6—8 hours at 160—170°; the product is treated with water, and crystallised from alcohol. *Bromocyanobenzyline*, $C_{24}H_{20}BrN_3$, the sole substitution product obtained by brominating cyanobenzyline, forms small, white crystals, and is converted into *bromo-4-hydroxy-5-phenyl-2 : 6-dibenzylmetadiazine*, $C_{24}H_{18}BrN_2OH$, when heated with strong hydrochloric acid at 140°; this melts at 120°.

*Chlorocyanobenzyline* forms pale yellow crystals, and melts at 65°. The *methiodide*, $C_{24}H_{21}N_3,MeI$, was prepared, and from it the *platinochloride*, $(C_{24}H_{20}MeN_3)_2,H_2PtCl_6$, but the corresponding base was not isolated. The action of methylic iodide on the hydroxy-derivative (m. p. 180°, *loc. cit.*) yielded the *methyl* derivative, $C_{24}H_{18}MeN_2{\cdot}OH$, which crystallises in white needles, and melts at 135°.

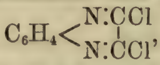
Cyanobenzyline (1 mol.) combines with acetic chloride (1 mol.) to form an additive compound, which melts at 116°, the corresponding benzoic chloride derivative melting at 129°. The cyanethine acetic chloride melts at 142°; cyanopropine acetic chloride at 210°. The additive compound of phenylcarbimide and cyanobenzyline melts at 162°.

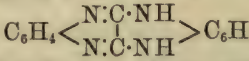
The action of nitrous acid on cyanobenzyline does not produce a compound analogous to that obtained by such treatment of cyanethine (Abstr., 1889, 685), but a *compound*, $C_{24}H_{15}N_3O_5.\frac{1}{2}H_2O$, which crystallises in yellow, felted needles, and melts at 210°. A. G. B.

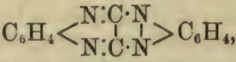
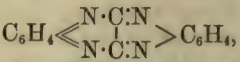
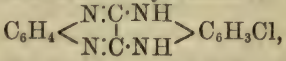
**Methyldioxytriazine (Acetoguanamide).** By Adriano Ostrogovich (*Gazzetta*, 1895, **25**, ii, 442—446).—On heating acetylurethane and carbamide in a closed tube at 148—150° for six hours, and crystallising the product from water, acetoguanamide is formed in accordance with the equation $COMe\cdot NH\cdot COOEt + CO(NH_2)_2 =$  $CO<\begin{matrix}NH\cdot CMe\\ NH\cdot CO-\end{matrix}>N$ $+ H_2O + EtOH$.

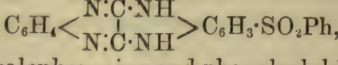
*Argentoacetoguanamide*, $C_4H_4N_3O_2Ag$, is a white flocculent powder.

W. J. P.

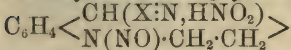
**Dichloroquinoxaline Derivatives.** By OSCAR HINSBERG and J. POLLAK (*Ber.*, 1896, **29**, 784—787).—Dihydroxyquinoxaline, prepared from orthophenylenediamine and oxalic acid, is converted into 2′ : 3′-*dichloroquinoxaline*,  $C_6H_4<\begin{matrix}N{:}CCl\\ \vert\\ N{:}CCl\end{matrix}$, by heating with phosphorus pentachloride at 160°; it is deposited from alcohol in colourless crystals, and melts at 150°.

*Fluoflavine*,  $C_6H_4<\begin{matrix}N{:}C\cdot NH\\ \vert\\ N{:}C\cdot NH\end{matrix}>C_6H_4$, is prepared by heating dichloroquinoxaline (1 mol.), orthophenylenediamine (2 mols.), and anhydrous sodium chloride at 120—130°, or by heating dihydroxyquinoxaline, or oxalic acid with orthophenylenediamine at 240°; the yield is about 50 per cent. of the theoretical, and less than that obtained by the first method. The compound crystallises from glacial acetic acid in deep yellow needles and melts at 360°. Its acetic acid solution is dark yellow with a yellowish-green fluorescence, sulphuric acid gives a yellow solution; in other media, it is insoluble. When boiled with soda and alcohol, it slowly dissolves giving a green liquid; it is stable towards reducing agents and acetic anhydride. The *hydrochloride*, $C_{14}H_{10}N_4,2HCl$, is yellow, and decomposes in presence of water.

*Quinoxalophenazine*,  $C_6H_4<\begin{matrix}N{:}C\cdot N\\ \vert\quad\vert\\ N{:}C\cdot N\end{matrix}>C_6H_4$, or  $C_6H_4\ll\begin{matrix}N\cdot C{:}N\\ \vert\\ N\cdot C{:}N\end{matrix}>C_6H_4$, is prepared by the oxidation of fluoflavine, preferably by means of glacial acetic acid and potassium dichromate; it crystallises from chloroform in reddish-brown plates or needles melting above 370°. When boiled with alcoholic soda, it gives a blue solution; it dissolves also in sulphuric acid with a brownish-yellow coloration, and on dilution the colour changes to brownish-red, and the *sulphate* is deposited; when heated with quinol, fluoflavine is regenerated and quinone is produced. When treated with concentrated hydrochloric acid, it is converted into *chlorofluoflavine*,  $C_6H_4<\begin{matrix}N{:}C\cdot NH\\ \vert\\ N{:}C\cdot NH\end{matrix}>C_6H_3Cl$, which is deposited from glacial acetic acid in yellow crystals, melts above 360°, closely resembles fluoflavine in general properties, and when oxidised yields a *chlorazine;* the stability of the chlorine atom indicates that it is present in one of the benzene rings.

*Phenylfluoflavylsulphone*,  $C_6H_4<\begin{matrix}N{:}C\cdot NH\\ \vert\\ N{:}C\cdot NH\end{matrix}>C_6H_3\cdot SO_2Ph$, prepared by the interaction of quinoxalophenazine and phenylsulphinic acid, in presence of glacial acetic acid, is a deep yellow, crystalline powder melting above 340°, its colour and fluorescence are stronger than those of fluoflavine; with alcoholic soda, it gives a yellowish-green solution, and when oxidised, it yields the corresponding phenazine.

J. B. T.

**Reduction Products of Cinchona Alkaloïds.** By Fritz Konek von Norwall (*Ber.*, 1896, **29**, 801—805).—The reduction of cinchonidine, quinine, and quinidine, is effected in the same manner as that of cinchonine (Abstr., 1895, i, 631), the resulting tetrahydro-bases are oily and readily yield nitroso-nitrites with the general formula,  $C_6H_4<\begin{matrix}CH(X{:}N,HNO_2)\\N(NO)\cdot CH_2\cdot CH_2\end{matrix}>$ $[X = C_{10}H_{16}O]$. These are converted by alkali into nitroso-bases which give Liebermann's reaction, but no coloration with chlorine, or bromine water. By the action of zinc and acid, resinous products are formed. The yield of nitrosonitrite from cinchonine is quantitative and from quinine very good, but from the others it is poor; this corresponds with the behaviour of the alkaloïds when oxidised.

*Tetrahydrocinchonidine nitrosonitrite* crystallises in yellow, lustrous needles melting and decomposing at 192—193°, but when rapidly heated the melting point is a few degrees higher; it is less soluble than the cinchonine derivative, and differs from it both in colour and in crystalline form. The *nitroso-base* is a yellow oil; the *methiodide* is pale yellow; the *hydrochloride* and *oxalate* are crystalline.

*Tetrahydroquinine nitrosonitrite* is at first the colour of peach blossom but quickly darkens and finally becomes pale yellow; it crystallises in glistening, yellow needles, melting and decomposing at 188°; when boiled for a few moments, nitrous anhydride is evolved and the liquid becomes olive green and gives, with ammonia, a red, flocculent precipitate. The *nitroso-base* is rose coloured.

*Tetrahydroquinidine nitrosonitrite* crystallises from water in deep yellow, lustrous needles, and from dilute alcohol in yellowish-brown prisms, melting at 178—179°. The *nitroso-base* is white and gives a blue coloration with phenol and sulphuric acid. J. B. T.

**Action of Heat on the Alkaloïds of Ipecacuanha.** By Benjamin H. Paul and Alfred J. Cownley (*Pharm. J. Trans.*, 1895, [4], **1**, 2).—Solutions of emetine and of cephaeline in excess of acetic acid can be boiled for a long time without change, but if they are evaporated in an open basin and the dry residue heated on a water bath for 16 hours, considerable darkening occurs, and there is a loss of alkaloïd, amounting to 27 per cent. in the case of emetine, and 22 per cent. in the case of cephaeline. The presence of air appears necessary for the alteration. R. R.

**Ipecacuanha.** By Richard A. Cripps (*Pharm. J. Trans.*, 1895, [4], **1**, 159—161).—Ipecacuanha was treated with ether and the residue extracted with rectified spirit. The alcoholic extract was evaporated, the residue extracted with chloroform while still acid, then made alkaline with ammonia and extracted with ether. The alkaloïd obtained in this way was dissolved in alcohol, an equal volume of ether added, and then more ether containing about 0·25 per cent. of hydrogen chloride, whereby a white precipitate was formed; the clear liquid was poured off, and more ethereal hydrogen chloride added in successive portions, until the whole of the alkaloïd had been precipitated in several fractions.

The 1st and 5th of these were taken for conversion into the aurochloride and platinochloride. The aurochlorides were found to be practically identical, and agreed with Paul's formula for emetine. Neither of the platinochlorides corresponded with that of cephaeline. It is concluded that the alkaloïd soluble in ether in this sample of ipecacuanha consisted solely of emetine. No trace of Arndt's volatile alkaloïd was detected. R. R.

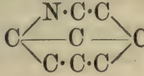
**Chelidonium Alkaloïds.** By N. A. Orloff (*Chem. Centr.*, 1895, ii, 226 and 305; from *Pharm. Zeit. Russ.*, **34**, 369—371 and 385—390).—Chelerythrine is contained in all parts of fresh specimens of *Chelidonium majus*, but none could be extracted from the dried plants. The fruit contains 0·06 per cent., and the root 0·001—0·005 per cent. of the alkaloïd. The plant is extracted with water containing a little sulphuric acid, the extract treated with potassium carbonate, and the washed and dried precipitate extracted with ether; the alkaloïd is then converted into the yellow, oily *sulphate*, and this is decomposed by means of ammonia. The *hydrochloride* is orange-yellow, but the base is colourless. *Chelilysine* is present both in the fresh and dried plants; these are extracted with water, the solution treated with soda, and the filtrate precipitated with tannin; the dried precipitate is then extracted with alcohol, the solution acidified with hydrochloric acid, and the hydrochloride further purified. It gives precipitates with platinic chloride, auric chloride, phosphotungstic acid, phosphomolybdic acid, and potassiobismuth iodide. The yield of hydrochloride is 0·007 per cent. The *base* is amorphous and almost insoluble in chloroform and ether. J. B. T.

**Scopoleïne.** By Walter Luboldt (*Chem. Centr.*, 1895, i, 546; from *Apoth. Zeit.*, 1894, **9**, 931—932; compare Abstr., 1895, i, 632).—*Tropylscopoleïne* is best prepared according to Liebermann and Limpach's method, by heating tropic anhydride with scopoline at 230°; the base may be extracted from the resulting brown mass by means of very dilute hydrochloric acid. It is also formed when scopoline is melted with tropide, or by the prolonged heating of natural scopolamine at 230°. The free base is a soft, amorphous substance, which melts at 166°; it is practically insoluble in water, readily soluble in chloroform and dilute acids, and only moderately in alcohol and ether. Neither the base itself nor its salts could be obtained in a crystalline form.

The *hydrobromide* is precipitated by ether from its alcoholic solution as a white, amorphous powder, which is extremely deliquescent. The *hydrochloride* is a yellowish, deliquescent, amorphous powder, which is readily soluble in water and alcohol. The *sulphate* and *nitrate* are sparingly soluble in alcohol; the *aurochloride* is a yellow, amorphous powder, sparingly soluble in boiling water, and melts at 180°; the *platinochloride* melts at 246—248°.

Analyses point to the composition $C_{17}H_{21}NO_4$ for the base, and it is therefore isomeric with the natural scopolamine. J. J. S.

**Alkaloïds from the Rind of Pomegranate Root.** By Giacomo L. Ciamician and Paul Silber (*Ber.*, 1896, **29**, 481—489; compare Abstr., 1892, 1110; 1893, i, 287; 1894, i, 154; 1895, i, 160).—The alkaloïds of the pomegranate root appear to be derived from a substance in which the carbon and nitrogen atoms are arranged as follows,

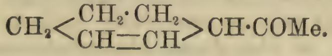


$$C\left<\begin{matrix}N\cdot C\cdot C\\ C\\ C\cdot C\cdot C\end{matrix}\right>C.$$

The authors propose to name the fundamental substances obtained in the course of their investigations as follows. Granatanine, $C_8NH_{15}$; granatenine, $C_8NH_{13}$; granatonine, $C_8NH_{13}O$; granatoline, $C_8NH_{14}\cdot OH$.

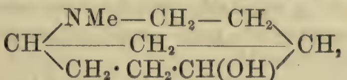
*Oxygranatanine*, $C_8NH_{15}O$, is formed by the action of alkaline permanganate on granatanine. The *hydrochloride* crystallises in slender, white needles, and melts and decomposes at 225°. The *platinochloride* decomposes at 230°. The *benzoyl derivative* melts at 69—70°.

When granatal (dihydrogranatone) is oxidised by means of alkaline permanganate, it is converted into normal adipic acid, which is identical with the acid prepared by other methods. The pure acid melts at 153—153·5° (corr.), and has the following crystallographic constants, which have not previously been determined; $a:b:c = 1·9637:1:1·79$; $\beta = 42° 55'$. Tropilene, the corresponding derivative in the tropine series, yields the same acid on oxidation. Granatal, therefore, appears to be tetrahydroacetophenone,



$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH{=}CH\end{matrix}>CH\cdot COMe.$$

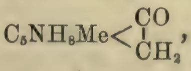
When methylgranatoline is submitted to oxidation, it is converted into *granatic* (*homotropinic*) *acid*, $C_9H_{15}NO_4$, which crystallises in small, colourless prisms, and melts and decomposes at 240—245°. The *aurochloride* melts and decomposes at 190°. This acid is very similar to tropinic acid, and is probably methylpiperidinecarboxyacetic acid. This would agree well with the formula proposed for methylgranatoline,



$$CH\left<\begin{matrix}NMe-CH_2-CH_2\\ CH_2\\ CH_2\cdot CH_2\cdot CH(OH)\end{matrix}\right>CH,$$

A. H.

**n-Methyltroponine.** By Giacomo L. Ciamician and Paul Silber (*Ber.*, 1896, **29**, 490—493).—Methylgranatoline is converted by oxidation into methylgranatonine, the corresponding ketone. In the same way tropine (methyltropoline) yields *methyltroponine*,



$$C_5NH_8Me<\begin{matrix}CO\\ |\\ CH_2\end{matrix},$$

which crystallises in long, broad, colourless needles, melting at 42°, and is deliquescent. The *aurochloride* melts at 163° with decomposition. *n-Methyltroponinoxime* crystallises in colourless prisms, melting at 115—116°. *n-Methyltroponine methiodide* forms large, colourless, cube-shaped crystals; when treated with sodium hydrogen carbonate, it yields dimethylamine and a liquid, which is probably a dihydrobenzaldehyde, $C_7H_8O$. This substance has a sharp odour of oil of bitter almonds, and boils at 70—72° (pressure = 14 mm). It appears to be identical with the substance obtained by Einhorn and Eichengrün from anhydroecgonine dibromide (Abstr., 1891, 65).

A. H.

**Solubility of Ferments and their Activity in Alcohol.** By A. DASTRE (*Compt. rend.*, 1895, **121**, 899—901).—Although relative insolubility in alcohol is generally employed as a means of isolating zymases, and although it has been recognised that some of them are not quite insoluble in even concentrated alcohol, there is at present little definite information on the subject.

The author finds that the digestive ferments and the ferments of the blood are quite insoluble in alcohol of 95°. With aqueous alcohol, the results are different. Trypsin is distinctly soluble in alcohol of from 10 to 25 per cent., but the solubility diminishes rapidly up to 50 per cent., and very rapidly beyond this point, becoming practically nil with 55 per cent. The amylolytic ferment of the pancreas is more soluble, and the solubility is distinct up to 65 per cent. alcohol. With the blood ferments, on the contrary, the solubility ceases to be recognisable with 4 or 5 per cent. alcohol.

Combining these with the previous observations of others, the ferments may be arranged in the following order of increasing solubility :—Blood ferments, emulsin, ptyalin, trypsin, pepsin, the ferment of *gaulteria*, the amylolytic ferment of the pancreas, myrosin.

The ferments remain active in the alcoholic solutions, but their effects are greatly retarded, because the attraction of the alcohol for the water is opposed to the essentially hydrolysing action of the ferments, and many of the digestible substances are insoluble in alcohol. With trypsin, digestive effects were observed with alcohol up to 15 per cent., and with the amylolytic ferment up to alcohol of 20 per cent.

C. H. B.

**Glycolysis.** By OTTO NASSE and FRIEDRICH FRAMM (*Pflüger's Archiv*, 1896, **63**, 203—208).—Lépine has stated that by the use of dilute sulphuric acid a diastatic can be converted into a glycolytic ferment. These experiments were repeated in the present research, with entirely negative results.

Diastatic ferments turn guaiacum tincture blue; this might account for the disappearance of some of the sugar, for sugar is easily oxidised. This action, however, is not due to the ferment itself, as it does not run parallel with ferment activity. Experiments, however, failed to substantiate the hypotheses.

W. D. H.

**The Chemical Nature of Diastase.** By THOMAS B. OSBORNE (*J. Amer. Chem. Soc.*, 1895, **17**, 587—603).—The author considers the old method for the preparation of diastase as unsatisfactory, but has used the following method with considerable success.

The proteïds are first separated from the carbohydrates and other substances by saturating the aqueous extract of malt with ammonium sulphate. By this means, the ferment and proteïds are precipitated together; the proteïd, existing as globulin, is then removed by dialysis, and the albumin and proteoses are separated as far as possible by fractional precipitation with alcohol.

In each case the diastatic power of the product was measured by Lintner's method. Lintner recommends extracting the malt with 20 per cent. alcohol, but the author finds that water is much better.

As a result of his investigations, the author comes to the conclusion that ordinary diastase contains (1) a globulin, (2) an albumin, and (3) probably two forms of proteose, one of which is precipitated by alcohol more readily than the albumin, whilst the other is less readily precipitated.

It is shown that the globulin, which is more readily rendered insoluble than the albumin, can be easily separated from the albumin by repeated precipitation by alcohol and dissolution in water. It is uncertain whether repeated fractional precipitation can be employed to completely separate the albumin from the proteoses. It may be that the proteose is a decomposition product of diastase. The albumin has most of the properties of leucosin, which the author has previously isolated from barley, wheat, and rye. It is also probable that the fermentable properties of diastase are due to the presence of this albumin, as the author finds that diastase containing the greatest percentage of coagulable albumin has the highest fermentable properties. If this albumin is identical with leucosin, it accounts for the fact that extracts of barley, wheat, &c., have a strong diastatic action on starch. The author, however, thinks it more probable that active diastase is a compound of albumin with proteose, and that it breaks up on heating, yielding coagulated albumin, and, further, that free albumin is also present, which has no diastatic power, but is coagulated at the same time. J. J. S.

**Action of Alcoholic Soda on Gelatin and Egg-albumin.** By CARL PAAL and WILHELM SCHILLING (*Chem. Zeit.*, 1895, **19**, 1487—1488).—The "proteïc acid," $C_8H_{16}N_2O_6$, obtained by W. Fahrion (*Chem. Zeit.*, **19**, 1000) by acting on silk, glue, &c., with caustic soda, is the hydrochloride of a peptone, such as has been described by Paal (compare Abstr., 1892, 895), and differs in character and composition according to its source. The "metallic salts" described by Fahrion are complicated mixtures of metallic chlorides, peptone hydrochlorides, free peptones, and metallic derivatives of peptones.
A. L.

**The Proteïds of the Rye Kernel.** By THOMAS B. OSBORNE (*J. Amer. Chem. Soc.*, 1895, **17**, 429—448).—Rye meal was exhausted with a solution containing 10 per cent. of sodium chloride, and the extract, after syphoning from the subsided insoluble matters, was freed from salts and globulin by dialysis in river water and by filtration; the solution then contained only those proteïds extracted from the seed which were soluble in pure water. These the author shows to be the same as those obtained from wheat meal, namely, an albumin, which he terms *leucosin*, and a proteose. The leucosin is obtained as a coagulum, on warming its aqueous solution to 63—65°, and agrees in composition and properties with that obtained from wheat. The proteïd which is soluble in saline solutions the author shows to be *edestin*, or vegetable vitellin (compare this vol., ii, 210).

Alcohol extracts a proteïd, *gliadin;* this is identical with the proteïd soluble in alcohol, which has previously been obtained from wheat (compare Abstr., 1893, i, 741). A proteïd, which is soluble in dilute potash solution, also occurs in rye meal, but the author was unable to obtain it in a pure state.

The amounts of the various proteïds present are given as, gliadin = 4·00, leucosin = 0·43, edestin and proteose = 1·76, proteïds insoluble in salt solution = 2·44 per cent. Total = 8·63 per cent. of the meal.

J. J. S.

**Method of obtaining Oxyhæmoglobin Crystals.** By MAURICE ARTHUS (*Compt. rend. Soc. Biol.*, 1895, **11**, 686).—If blood corpuscles dissolved in water are introduced into a dialysing tube, and this is plunged into dilute alcohol (20—25 per cent.), after 24 hours crystals form inside the tube, sometimes large enough to be visible to the naked eye.

W. D. H.

**Phrenosin—an immediate Educt from the Brain—and the Products of its Chemolysis by Nitric acid.** By JOHN L. W. THUDICHUM (*J. pr. Chem.*, 1896, [2], **53**, 49—91).—The author discusses at length the "protagon hypothesis," with special reference to the paper of Kossel and Freytag on the subject (Abstr., 1893, i, 235). He complains that these physiologists have distorted the history of the isolation of nerve educts (compare Abstr., 1882, 235, 537), and have misapplied the name cerebrin to phrenosin. The facts with regard to the "chemolysis" of phrenosin by nitric acid are as follows. At least five products are obtained. (1) Neurostearic acid (Abstr., 1882, 537), which is not identical with stearic acid, as Kossel and Freytag state. (2) *Phrenylin*, a new product, which is insoluble, or very slightly soluble in ether, but soluble in boiling alcohol, from which it separates in the form of a white, microcrystalline mass; it melts gradually between 115° and 130°. This substance yields the oleocholide reaction in a hitherto unnoticed manner; the purple colour is not in solution, but belongs to suspended particles, which become colourless when dehydrated by fresh sulphuric acid; the hydrated particles are insoluble in dry chloroform, but dissolve in the hydrated solvent; the nitrogen content of phrenylin and its oleocholide reaction indicate that it is a product from the same radicle which yields sphingosine when phrenosine is "chemolysed" with sulphuric acid (*loc. cit.*). Phrenylin is apparently a neutral substance, although it shows a tendency to retain barium, as the cerebrosides do. (3) Mucic acid, which is a product of the oxidation of cerebrose (*loc. cit.*). These three compounds form the chief products of the "chemolysis;" but in addition there were isolated (4) a red-coloured resin acid, and (5) a neutral compound, freely soluble in ether, not capable of combining with baryta, and giving the oleocholide reaction.

A. G. B.

# Organic Chemistry.

**Composition of Marsh Gas.** By TH. SCHLOESING, jun. (*Compt. rend.*, 1896, **122**, 398—400).—Sixteen samples of marsh gas, mostly from French coal mines, but some from ditches, contained: methane 55·6 to 96·9 per cent., nitrogen 2·2 to 39·8 per cent., oxygen 0·0 to 0·8, and carbonic anhydride 0·0 to 4·1. As a rule, the proportion of methane is more than 80 per cent. The quantity of oxygen and carbonic anhydride is usually very small, and in most cases, though not in all, these gases have been introduced during the process of collecting. The proportion of nitrogen varies widely, and is sometimes relatively high; it contains the same proportion of argon as atmospheric nitrogen does, and has most probably been derived from the air, the oxygen having been removed by combination with constituents of the coal. C. H. B.

**Action of Bromine on Tertiary Alcohols of the Series $C_nH_{2n+2}O$.** By WLADIMIR IPATIEFF (*J. pr. Chem.*, 1896, [2], **53**, 257—287).—The published researches on the chlorination of hydrocarbons of the $C_nH_{2n}$ series show that when such hydrocarbons are of the types $R_2C{:}CH_2$, $R_2C{:}CHR$ and $R_2C{:}CR_2$ they yield unsaturated chlorinated derivatives of the form $C_nH_{2n-1}Cl$, hydrogen chloride being evolved; the hydrocarbons of the types $RHC{:}CH_2$ and $R'HC{:}CHR$, however, yield dichlorides, $C_nH_{2n}Cl_2$, without separation of hydrogen chloride. The bromination of the ethylenes appears to produce a dibromide in every case, although Faworsky has shown that the dibromide is by no means always the sole product.

The work of Étard (Abstr., 1892, 809) has established the similarity between the action of chlorine and that of bromine on primary and secondary alcohols, but the behaviour of tertiary alcohols with bromine has received but little notice. The author finds that when dimethylethylcarbinol is left in contact with bromine (1 mol.) at the normal, or at slightly lower, temperature, no action occurs for some hours, but presently it begins and proceeds so rapidly that the mixture explodes. By heating the carbinol at 50—56°, the action takes place sufficiently rapidly for each drop of bromine to disappear as it falls from the dropping-funnel, and the bromination may be conducted with safety. After all the bromine has been added, and the flask has been left at rest for a day, two layers have formed, the lower of which is the brominated product; it is washed with sodium carbonate solution, dried, and fractionally distilled at 16 mm. pressure. The chief product (77 per cent.) distils at 64—66°, and is amylenic dibromide, $CMe_2{:}CBr{\cdot}CHMeBr$; its sp. gr. = 1·7005 at 0°/0°; and its constitution is settled by the fact that when heated with lead oxide and water it yields methyl isopropyl ketone, and further by its behaviour with alcoholic potash, by which it may be successively converted into bromotrimethylethylene $CMe_2{:}CMeBr$ (b.p. 118°; sp.gr.,

= 1·3073 at 0°/0°), and dimethylisoallylene, $CMe_2\!:\!C\!:\!CH_2$ (b. p. 39·5—41°); it must contain a small proportion of the dibromide,

$$CH_2Br\cdot CMeBr\cdot CH_2Me,$$

for a little methylethylacetaldehyde is found in the product of both the above reactions. A tertiary amylic bromide and a tribromopentane are the other products of the bromination of dimethylethylcarbinol.

Contrary to the statement of Jawein (*Annalen*, **195**, 255), the author finds that dimethylpropylcarbinol can be prepared in quantity (50 per cent.) by Butleroff's method from zinc methide and butyric chloride. It was treated with bromine in the manner described above, and was found to yield small proportions of a tertiary hexylic bromide and tribromohexane, but chiefly (70 per cent.) hexylene dibromide, $CMe_2Br\cdot CHBr\cdot CH_2Me$ (sp. gr. = 1·6196 at 0°/0°) together with a little of the dibromide $CH_2Br\cdot CMeBr\cdot CH_2\cdot CH_2Me$. The first of these two dibromides was converted into a bromohexylene (b. p. 138—141°; sp. gr. = 1·2491 at 0°/0°), and a *hydrocarbon*, $C_6H_{10}$ (b. p. 71—73°, uncorr.; sp. gr. = 0·73033 at 0°/0°), by treatment with alcoholic potash.

Three bromine derivatives are similarly obtained by brominating triethylcarbinol, namely a tertiary hexylic bromide, a heptylene dibromide (55 per cent.) and a tribromoheptane. It seems, therefore, that this is the general course of the action of bromine on tertiary alcohols, the proportion which the three products bear to each other being dependent on the temperature at which the action takes place.

The paper contains details of the method which the author has found most suitable for preparing considerable quantities (300—400 grams) of zinc methide from zinc and methylic iodide at one operation. A. G. B.

**Action of Nitric acid on Potassium Cobalticyanide.** By C. Loring Jackson and Arthur M. Comey (*Ber.*, 1896, **29**, 1020—1022).—When a concentrated solution of potassium cobalticyanide is boiled with an equal volume of strong nitric acid, it becomes coloured red after some minutes and then forms a semisolid gelatinous mass, which dissolves slowly in water at 60° when it has been freed from impurities by washing. This substance after drying in a vacuum has the composition, $KH_2Co_3(CN)_{11} + H_2O$. The amorphous mass obtained by the evaporation of its solution in water, is converted into a red powder by treatment with cold water. The solution has acid properties and yields precipitates with the solutions of various metallic salts. The *silver salt* is a pale red, amorphous mass of the formula $Ag_3Co_3(CN)_{11} + H_2O$, whilst the *barium salt* has the formula $BaHCo_3(CN)_{11} + 1\frac{1}{2}H_2O$. The free *cobaltocobalticyanic acid* is prepared in a similar manner from cobalticyanic acid and closely resembles the potassium salt, but is less stable. Potassium ferricyanide appears to yield a somewhat similar substance when it is treated in the same manner, but this has not yet been carefully examined. A. H.

**New Mode of Formation of Nitroprussides.** By C. MARIE and R. MARQUIS (*Compt. rend.*, 1896, **122**, 473—474).—When potassium ferricyanide in aqueous solution is acted on by nitrous acid liberated from sodium nitrite by carbonic anhydride, it is completely converted into the ferrocyanide, and only traces of nitroprusside are formed. On the other hand, when potassium ferrocyanide is treated in the same way, it is largely converted into the nitroprusside, the reaction being limited by the reversing action of the alkali carbonate that is formed. With calcium ferrocyanide, inert calcium carbonate is formed, and the change into nitroprusside is complete. C. H. B.

**Methylic Alcohol, Acetic acid, and Carbon from various Woods.** By ERNEST BARILLOT (*Compt. rend.*, 1896, **122**, 469—471).—Fractionation of the crude product of the destructive distillation of various woods shows that for 100 kilos. of wood the yield of acetic acid varies from 3·72 to 6·40 kilos., of methylic alcohol from 1·27 to 2·15 litres, and of charcoal from 20·62 to 26·0 kilos. A mixture of oak, beech, and hornbeam gave the best yield of the alcohol. White woods are, as a rule, to be avoided for the production of charcoal. C. H. B.

**Constitution of Glycols formed by the Action of Caustic Potash on Aldehydes.** By ADOLF LIEBEN (*Monatsh.*, 1896, **17**, 68—75).—The constitution assigned by Fossek (Compare Abstr., 1884, 37) to the glycols obtained by acting on mixtures of isobutyric with other aldehydes, is not that which is to be expected if the rule of Lieben and Zeisel be applied. The latter requires the initial production of an unsaturated aldehyde in the following manner:

$$R\cdot CH_2\cdot CH{:}O + R'\cdot CH_2\cdot CH{:}O = R\cdot CH_2\cdot CH{:}CR\cdot CH{:}O + H_2O.$$

In the case of isobutaldehyde, where the tertiary carbon attached to the aldehydic group is incapable of yielding an unsaturated compound in the above fashion, a hydroxy-aldehyde or aldol should be the initial product, the subsequent production of a glycol resulting from the reducing action of the caustic potash.

In order to decide between the two views, experiments have been undertaken with the object of ascertaining if glycols are produced when aldehydes other than those of the isobutyric type are used, and the results are in favour of the latter view.

The author discusses the experiments of Just and Franke (compare the two following abstracts) in relation to the above hypotheses, and mentions that similar experiments are being made in which caustic soda is substituted for potash. A. L.

**Action of Alcoholic Potash on a Mixture of Formaldehyde and Isobutaldehyde.** By ALEXANDER JUST (*Monatsh.*, 1896, **17**, 76—84).—The action of alcoholic potash on a mixture of isobutaldehyde and formaldehyde results in the production of isobutyric acid and a glycol, $C_5H_{12}O_2$. The latter is doubtless identical with the glycol obtained by Apel and Tollens (compare Abstr., 1894, i, 353) by the action of calcium hydroxide on the same mixture of aldehydes;

it is very hygroscopic, dissolves readily in water, ether, alcohol, chloroform, and hot benzene, crystallising from the latter in beautiful needles; it boils at 206° under 747 mm. pressure, and melts at 127°. The *diacetate* boils at 212° under 740 mm. pressure. The glycol, on oxidation with potassium permanganate, yields acetone and a mixture of two acids, one dimethylmalonic acid, and the other in all probability hydroxytrimethylacetic acid, as the former is obtained from it by oxidation.

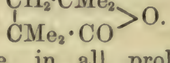
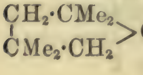
From these results it is seen that the above action may be expressed by the equation

$$CH_2O + 2CHO\cdot CHMe_2 + KOH = CMe_2(CH\cdot OH)_2 + COOK\cdot CHMe_2.$$

A. L.

**Action of Alcoholic Potash on Isobutaldehyde.** By ADOLF FRANKE (*Monatsh.*, 1896, **17**, 85—101).—The glycol obtained by Fossek (Abstr., 1882, 1279) by the action of alcoholic potash on isobutaldehyde, when treated with cold, concentrated sulphuric acid, yields only a small quantity of oil, the bulk of the product consisting of a *glycolic hydrogen sulphate*, which may be isolated by means of its *barium* salt. The latter crystallises in silky, colourless needles, dissolves readily in water, decomposes at 70—80° with production of barium sulphate, and, when heated with somewhat dilute sulphuric acid, yields the oily product described by Fossek and Swoboda (see Abstr., 1891, 31). The latter may be directly prepared from the glycol by the action of boiling dilute sulphuric acid, and, as stated by its discoverers, may be separated by distillation into a low-boiling and a high-boiling portion of the compositions, $C_8H_{16}O$ and $C_{16}H_{32}O_2$ respectively. The low-boiling portion is a saturated compound, does not interact with acetic anhydride, phenylhydrazine or hydroxylamine, and does not combine with water at 130—140°; it is therefore an oxide, comparable with ethylenic oxide, inexplicable by means of Fossek's formula for the glycol.

The glycol is slowly oxidised by cold, dilute potassium permanganate, yielding diisopropyl ketone, $CO(CMe_2)_2$, and the hydroxy-acid $C_8H_{16}O_3$, obtained by Fossek (*loc. cit.*). The latter yields diisopropyl ketone on oxidation, and is therefore trimethyl-2 : 2 : 4-pentanol-3-oic acid, $COOH\cdot CMe_2\cdot CH(OH)\cdot CHMe_2$; hence the glycol is trimethyl-2 : 2 : 4-pentane-1 : 3 diol, $OH\cdot CH_2\cdot CMe_2\cdot CH(OH)\cdot CHMe_2$.

The oxide, $C_8H_{16}O$, is oxidised by dilute acid permanganate to an acid, either acetic or dimethylmalonic acid, and a volatile *substance*, $C_{10}H_{14}O_2$, which separates from ether in long, prismatic, channelled crystals, is volatile in steam, melts at 42°, and boils without decomposing at 205°; when boiled with calcium hydroxide, it yields a *calcium* salt, $(C_8H_{15}O_3)_2Ca$, forming a colourless, crystalline mass, and is therefore the lactone of a γ-hydroxy-acid, $C_8H_{16}O_3$, and has the constitution  $\begin{matrix}CH_2\cdot CMe_2\\ | \\ CMe_2\cdot CO\end{matrix}\!>\!O$. The oxide, whence the lactone is derived, is therefore, in all probability, a 1 : 4-oxide of the structure  $\begin{matrix}CH_2\cdot CMe_2\\ | \\ CMe_2\cdot CH_2\end{matrix}\!>\!O$, produced from the 1 : 3-glycol by the initial production, under the influence of the sulphuric acid, of a 3 : 4-unsaturated alcohol.

The oil of high boiling point, $C_{16}H_{32}O_2$, obtained simultaneously with the above oxide, proves to be an ether, being decomposed by fuming hydrobromic acid at 100°, with production of brominated compounds which readily lose hydrogen bromide on distillation, whilst by the action of dilute sulphuric acid at 100°, it is partially decomposed, the oxide, $C_8H_{16}O$, being formed. It is probably, therefore, a ditetramethyltetramethylene dioxide. A. L.

**Condensation of Formaldehyde with Anhydro-enneaheptitol.** By M. Apel and O. Witt (*Annalen*, 1896, **290**, 153—155 ; compare this vol., i, 115).—*Anhydro-enneaheptitol diformal*, $C_{11}H_{18}O_6$, is obtained from formaldehyde and anhydro-enneaheptitol under the influence of hydrochloric acid; it occurs in two modifications, which melt at 165° and 207° respectively. The same *acetate* is produced from both sources, and melts at 107°. M. O. F.

**Galactitol, from Yellow Lupin Seed.** By C. Heinrich L. Ritthausen (*Ber.*, 1896, **29**, 896—899).—*Galactitol*, $C_{19}H_{18}O_7$, is obtained by extracting lupin seed with dilute alcohol (80 per cent.), evaporating the solution to dryness, and purifying the residue from fat, lupinine, and lupinidine; it crystallises in thin colourless, hexagonal, hemihedral plates belonging to the rhombic system, $a : b : c = 0{\cdot}5068 : 1 : 0{\cdot}7332$; $\beta = 1{\cdot}52$; the compound softens at 138°, melts at 140—142°, is tasteless, and optically inactive. The yield is 1·05 per cent. of the seed employed. When hydrolysed by means of dilute sulphuric acid, galactitol yields more than 60 per cent. of galactose, which was fully identified. J. B. T.

**Action of Fuming Nitric acid on Xylose and on Arabinose.** By Richard Bader (*Chem. Zeit.*, 1895, **19**, 1851 ; compare this vol., i, 335).—The author has further examined the white, hygroscopic mass obtained on treating xylose with fuming nitric acid, which was thought to be xylotrihydroxyglutaric anhydride. The mass usually contains 0·2—1·5 per cent. of nitrogen due to impurities; it was found impossible to obtain either the acid itself, or its ammonium or silver salt, in a state of purity, from the anhydride; by careful working, however, a barium salt was obtained, which yielded numbers agreeing with those required for barium trihydroxyglutarate.

Arabinose treated in the same way yields arabinotrihydroxyglutaric anhydride, but none of the derivatives of the acid could be obtained in a pure form. J. J. S.

**Isomaltose.** By Ed. Jalowetz (*Chem. Zeit.*, 1895, **19**, 2003 ; compare Ling and Baker, Trans., 1895, 704 ; Brown and Morris, *ibid.*, 709 ; H. Ost, *Chem. Zeit.*, 1895, **19**, 1501 ; and Ulrich, this vol., i, 335).—The author shows that pure maltose, when mixed with varying quantities of dextrin, yields osazones, which not only differ in melting point, but also in their general appearance and crystalline form. With equal quantities of maltose and dextrin an osazone is obtained, which melts at 150—155°, but the melting point alters after several recrystallisations.

These results agree with those of the authors mentioned, and speak against the existence of Lintner's isomaltose. J. J. S.

**Behaviour of Basic Lead Acetate towards Sugar Solutions.** By HANNO SVOBODA (*Zeits. Ver. Rübenzucker-Ind. Deut. Reichs.*, 1896, **46**; Heft 481, 29 pages).—When 20 per cent. sugar solutions are treated for 24 hours with lead acetate (1 vol.), the solutions become coloured, as follows: maltose, red; galactose, orange; levulose, yellow; dextrose, bright yellow; lactose, yellowish; there is also a decrease in polarisation, most in the case of galactose (53 per cent.), least with maltose; cane sugar, and raffinose are not decomposed, but when more lead oxide than usual is present, raffinose is precipitated. The amount of lead oxide in solution, to which the action is due, may be estimated by treating with excess of titrated sulphuric acid for three hours, and then titrating back with sodium hydroxide.

As regards the effect of lead acetate on the rotatory power of sugars, that of cane sugar is at first slightly diminished, then raised, and, finally, diminished. The rotatory power of maltose is slightly lessened, that of raffinose, lactose, galactose, and levulose considerably diminished, according to the amount of lead acetate added. When the lead solution is slightly acidified with acetic acid, a slight alteration of rotatory power is produced. Addition of increasing amounts causes, with (1) cane sugar and dextrose, a slight constant increase; (2) levulose, at first a slight diminution, then an increase; (3) lactose, maltose, galactose, and raffinose, a slight diminution of rotatory power. The changes in rotatory power are due to the formation of soluble lead sucrates; these compounds are precipitated by much alcohol, and contain lead oxide, 66·5—73·6; sugar, 10·9—16·7; and acetic anhydride, 13·6—16·5 per cent. They are not true sucrates, as they contain acetic acid, but compounds of sugar with basic lead acetate. Beythien and Tollen's trilead raffinosate contains 10 per cent. of acetic anhydride (*Zeits. Ver. Rübenzucker-Ind.*, 1889, 748 and 906; Abstr., 1890, 580). Aqueous solutions of the sucrates behave, as regards rotation, very similarly to the sugar solutions containing lead acetate.

A mixture of dilute lead acetate solution and an equal bulk of 3 per cent. ammonia precipitates sugar from aqueous solutions. The cane sugar precipitate is free from ammonia, and contains 2·85 per cent. of acetic anhydride.

The filtrate obtained from a solution of lead acetate after treatment with sufficient baryta, strontia, or lime to decompose the neutral lead acetate, precipitates sparingly soluble lead sucrates from sugar solutions. Magnesium hydroxide does not have this effect, but a magnesia precipitant is obtained by digesting magnesium acetate (20 grams) in water (100 c.c.) with litharge (20 grams). The precipitating power of these solutions is proportional to the amount of basic lead oxide present; and this depends on the strength of the base, being greatest in the case of magnesia, least with baryta. Zinc lead acetate does not precipitate more than lead acetate. The precipitates are free from baryta, strontia, &c., and contain, besides sugar and lead, acetic acid (3·4—4·7 per cent.). The magnesia lead acetate solution (9 grams of lead oxide per c.c.) precipitates, from 20 per cent. solutions, 75 to 100 per cent. of sugar, according to the nature of the sugar, and thus forms a method for isolating and identifying different sugars.

The precipitation of sugar from solutions containing sulphates, chlorides, &c., on adding lead acetate, is explained thus:—With sugars, basic lead acetate forms various sucrates which dissolve readily in lead acetate, but only sparingly in water. Salts which react with lead acetate to form insoluble lead compounds precipitate the sucrates by precipitating the solvent. N. H. J. M.

**Preparation of Fatty Amines.** By AUGUSTE TRILLAT (*Bull. Soc. Chim.*, 1895, [3], **13**, 689—692).—The author does not agree with the conclusions of Brochet and Cambier (Abstr., 1895, i, 325) that in the preparation of methylamine from formaldehyde and ammonium chloride the presence of a reducing agent does not hasten the reaction. By working with a mixture of formaldehyde, ammonia, and hydrochloric acid in the presence of a small quantity of zinc, he has been enabled to obtain the methylamine in the space of a few minutes. Ethylamine results from the reduction of aldehydammonia, and not pyridine bases as stated by the above-mentioned investigators.

J. F. T.

**Reduction of Methylnitramine and Ethylnitramine.** By JOHANNES THIELE and CARL MEYER (*Ber.*, 1896, **29**, 961—963).—Thiele and Lachman have suggested (this vol., i, 207) that when reduced, methylnitramine is first converted into nitrosomethylamine and then into diazomethane. β-Methoxynaphthalene is produced by the interaction of methylnitramine, β-naphthol, and aluminium in alkaline solution, thus indicating the production of diazomethane; but the isolation of this from aqueous solution is practically impossible. When reduced as above, without β-naphthol, the liquid on acidifying evolves nitrogen (about two-sevenths of the theoretical), and rapidly reduces metallic salts. Nitrous acid is only present in traces. When reduced by means of hydrochloric acid and zinc dust, methylnitramine is converted into hydrazine, methylhydrazine, and methylamine. The yield of methylhydrazine is poor. Ethylnitramine, under the same conditions, gives ethylhydrazine, the yield being slightly better. Methylnitramine is obtained from dinitrodimethyloxamide which is readily prepared by mixing dimethyloxamide (20 grams) with common nitric acid (50 c.c.), adding distilled sulphuric acid (100 c.c.), and treating the crystals with ice. The yield is 99—100 per cent. of the theoretical. J. B. T.

**Oxidation of Crotonaldehyde.** By ER. CHARON (*Compt. rend.*, 1896, **122**, 533—535).—Crotonaldehyde, prepared by the methods of Lieben and of Newbury and Orndorff, does not appear to have a definite boiling point; it therefore seemed interesting to ascertain whether the product was a homogeneous substance, or whether it was a mixture of the two possible stereoisomerides.

The aldehyde was, therefore, oxidised by means of silver oxide, and was found to give the acid melting at 71°; even on separating the aldehyde into two fractions and oxidising them separately, the same acid was in each case produced, the yield being 90 per cent. of the theoretical. The acid melting at 71° was also obtained on allowing the aldehyde to oxidise slowly in the air. J. F. T.

**Disubstituted Amidoacetones.** By RICH. STOERMER and W. POGGE (*Ber.*, 1896, **29**, 866—874; compare Abstr., 1895, 681).—*Dipropylamidoacetone*, $NPr_2\cdot CH_2\cdot COMe$, boils at 188°, and has the sp. gr. 0·8337 at 14°. The *hydrochloride* forms white, lustrous plates; the *platinochloride* melts at 175—176°, the *aurochloride* at 95—96°. The *methiodide* crystallises in white needles melting at 234°; the *oxime* is an oil which could not be obtained crystalline, and the *hydrazone* is also an oil. The *semicarbazone* is a microcrystalline powder melting at 110°.

*Methylpropylamidoacetone* is formed by the distillation of the quaternary hydroxide obtained from the methiodide of the foregoing base. It boils at 129°, has a smell resembling that of peppermint, and forms a *platinochloride* which melts at 169—170°.

*Diisobutylamidoacetone* boils at 206—207°, and becomes yellow when kept; its sp. gr. is 0·8735 at 15°. The *platinochloride* melts at 176—177°, the *aurochloride* at 145°, the *hydrochloride* at 276°, the *hydrobromide* at 279°, and the *hydriodide* at 281°. The last three salts are all soluble in water, but are not hygroscopic. The *methiodide* forms small, lustrous crystals, and melts at 288°, whilst the *semicarbazone* melts at 132°. *Methylbutylamidoacetone* boils at 154—155°; the *platinochloride* melts at 149—150°. *Diisoamylamidoacetone* boils at 219—220°, and has the sp. gr. 0·8911 at 17°. The *hydrochloride* melts above 290°; the platinochloride and aurochloride could not be prepared, since the solutions of these chlorides are immediately reduced by the base. The *methiodide* melts above 290°. The *oxime* crystallises in lustrous, white plates; the *semicarbazone* melts at 166°.

*Methylamylamidoacetone* boils at 175—176°; the *platinochloride* melts at 139—140°. When the methiodide of this base is converted into the hydroxide and distilled, dimethylamidoacetone is formed.

The solubility of the bases and their hydrochlorides in water decreases as the molecular weight rises. A. H.

**Melting and Solidifying Points of some Fatty acids.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1895, [3], **13**, 758—759).—By the use, for temperatures down to −55°, of methylic chloride, and below this of a mixture of solid carbonic anhydride and ether, the following constants have been determined.

| | Melting point. | Solidifying point. |
|---|---|---|
| Propionic acid ........ | −36·5° | −40° |
| Normal valeric acid ... | −58·5 | −64 |
| Isobutyric acid........ | −79·0 | −82 |
| Isovaleric acid ........ | −51·0 | −57 |

J. F. T.

**Existence of a Sulphur Compound in Cotton-seed Oil.** By J. DUPONT (*Bull. Soc. Chim.*, 1895, [3], **13**, 696—697).—The author considers the well-known action of cotton-seed oil on silver nitrate solutions, not to be due to reduction, and therefore deposition of metallic silver, but to the presence of a sulphur compound in the oil, and the consequent precipitation of silver sulphide.

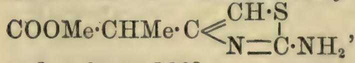
On distillation with steam and extraction of the distillate with ether, cotton-seed oil yields a powerfully smelling product, which, when oxidised with nitric acid and treated with barium chloride, gives a copious precipitate of barium sulphate.

In this manner, 5 grams of cotton-seed oil were found to contain 0·021 gram of sulphur. The compound is, however, only slightly volatile, for although this sample had been distilled with a quantity of steam corresponding with 2 litres of water, yet the residual oil still gave the silver nitrate reaction. J. F. T.

**Halogen Substitution Derivatives of Ethylic Acetoacetate.** By MAX CONRAD (*Ber.*, 1896, **29**, 1042—1048.) With L. SCHMIDT.—When ethylic acetoacetate, dissolved in carbon bisulphide, is treated with bromine at the ordinary temperature, the mixture allowed to remain, and then poured into water, the product consists entirely of ethylic γ-bromacetoacetate. If, on the other hand, the mixture is immediately freed from hydrobromic acid by agitation with water, a mixture of the α- and γ-bromo-compounds is obtained. This probably accounts for the results obtained by Nef (Abstr., 1892, 140) and other chemists. Ethylic α-bromacetoacetate, on the other hand, is obtained pure by the action of bromine on ethylic acetoacetate mixed with double its volume of water, and cooled by ice. The α-compound is not converted into the γ-derivative by distillation under reduced pressure, and does not yield ethylic succinosuccinate when treated with sodium ethoxide.

Ethylic α-chloracetoacetate does not appear to be converted into the γ-compound even when left in contact with hydrogen chloride for a protracted period. *Ethylic αα-chlorobromacetoacetate* is formed when chlorine is passed into ethylic α-bromacetoacetate, and is a colourless oil. Ammonia converts it into chlorobromacetamide, which melts at 117°. Ethylic αα-dibromacetoacetate reacts with 2 mols. of thiocarbamide to form ethylic μ-amidomethylthiazolecarboxylate.

With ANTON KREICHGAUER.—The behaviour of methylic methylacetoacetate towards bromine is similar to that of ethylic acetoacetate, the γ-bromo-compound being obtained when the product is allowed to remain in contact with hydrogen bromide for some time. It is a colourless oil, the vapour of which irritates the eyes. When heated for some hours on the water bath, it is converted into tetric acid. With thiocarbamide, it yields *methylic μ-amidothiazylpropionate*,



$COOMe\cdot CHMe\cdot C\!<\!\begin{array}{l}CH\cdot S\\ \quad\;\;|\\ N{=}C\cdot NH_2\end{array}$, which crystallises in colourless prisms, and melts at 130°.

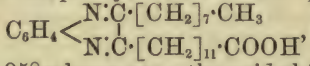
*Methylic α-bromomethylacetoacetate* is formed when the bromination is carried out at 0° and in presence of water. It is an oil which does not react with thiocarbamide. When kept, it gradually changes into the γ-derivative. A. H.

### Relation between Derivatives of Ricinoleic and Oleic acids.

By Otto Behrend (*Ber.*, 1896, **29**, 806—809).—*Bromoketostearic acid*, $CH_3\cdot[CH_2]_5\cdot CHBr\cdot CH_2\cdot CH_2\cdot CO\cdot[CH_2]_7\cdot COOH$, can be prepared in the same way as chloroketostearic acid (Abstr., 1895, i, 647); it melts at 55°, and, when recrystallised from acetic acid or alcohol, is slowly reconverted into hydroxyketostearic acid, hydrogen bromide being given off.

Chloroketostearic acid is reduced by hydriodic acid at 180° to stearic acid. It is reduced by zinc and hydrochloric acid at 80—90° to a *ketostearic acid*, which melts at 83°, and must have the constitution $CH_3\cdot[CH_2]_8\cdot CO\cdot[CH_2]_7\cdot COOH$, for it yields an oxime, and this undergoes the Beckmann transformation, yielding an amide (possibly a mixture of stereoisomeric varieties, for it melted at 75—85°) which on hydrolysis gave nonylamine, $CH_3\cdot[CH_2]_8\cdot NH_2$, and azelaic acid, $COOH\cdot[CH_2]_7\cdot COOH$, and also capric and amidocaprylic acids, $CH_3\cdot[CH_2]_8\cdot COOH$ and $NH_2\cdot[CH_2]_7\cdot COOH$. This ketostearic acid is isomeric with that prepared by Baruch from stearolic acid (Abstr., 1894, i, 170). C. F. B.

### Constitution of Behenoxylic and Stearoxylic acids.

By A. Spieckermann (*Ber.*, 1896, **29**, 810—813).—Ketoketoximebehenic acid (Abstr., 1895, i, 208), which melts, when pure, at 85—86°, undergoes the Beckmann transformation, and yields *pelargylamidobrassylic acid*, $CH_3\cdot[CH_2]_7\cdot CO\cdot NH\cdot CO\cdot[CH_2]_{11}\cdot COOH$. This melts at 116°, and can be hydrolysed into ammonia and pelargonic and brassylic acids, $CH_3\cdot[CH_2]_7\cdot COOH$ and $COOH\cdot[CH_2]_{11}\cdot COOH$. Behenoxylic acid must, therefore, be $CH_3\cdot[CH_2]_7\cdot CO\cdot CO\cdot[CH_2]_{11}\cdot COOH$, and, as we should expect from such a compound, it does actually yield, with orthophenylenediamine, a quinoxaline (*octylquinoxalinedodecoic acid*,  $C_6H_4<\begin{array}{l}N\colon C\cdot[CH_2]_7\cdot CH_3\\ \quad\;\; |\\ N\colon C\cdot[CH_2]_{11}\cdot COOH\end{array}$, melting at 45°). Behenoxylic acid melts at 95° when pure; the acid obtained as a bye-product in its preparation, and formerly supposed to be behenic acid, has now been identified as arachidic acid.

Stearoxylic acid is shown in a similar manner to have the constitution $CH_3\cdot[CH_2]_7\cdot CO\cdot CO\cdot[CH_2]_7\cdot COOH$, for it yields a *ketoketoxime acid*, melting at 76—81°, and this undergoes the Beckmann transformation into *pelargylamidoazelaic acid*,

$$CH_3\cdot[CH_2]_7\cdot CO\cdot NH\cdot CO\cdot[CH_2]_7\cdot COOH,$$

which can be hydrolysed to ammonia, pelargonic acid, and azelaic acid, $COOH\cdot[CH_2]_7\cdot COOH$. C. F. B.

### Derivatives of Ethylic Acetoacetate.

By Carl Boettinger (*Arch. Pharm.*, 1896, **234**, 87—91).—An *oil*, probably

$$O[CH(COMe)\cdot COOEt]_2,$$

was prepared in the following manner. Strong sulphuric acid (several drops) is added at intervals of a day to a mixture of equal weights of glyoxylic acid and ethylic acetoacetate, until 7 c.c. has been added in all; after 10 days ether is added, and the solution washed with water. The ethereal solution is evaporated, and the residual oil is shaken with water; this aqueous solution leaves a yellow syrup when evaporated, and this is completely soluble in cold water; the solution reduces ammoniacal silver nitrate, and contains an acid which has not been isolated in a pure form. The oil remaining undissolved by the water is heated with a solution of lead acetate, and the product extracted with ether, whereby a white lead salt is obtained which gives a vapour smelling of ethylic acetate when heated with strong sulphuric acid; a yellow barium salt is formed when the oil is treated with baryta water. The oil is viscid, colourless, and difficultly solidified; when heated, it gives a pungent vapour; aqueous ammonia hardly dissolves it at all, and in water it is insoluble; with bromine, it yields a product which is insoluble in dilute soda, but gives an odour of carbylamine when heated with aniline and sodium hydroxide. With phenylhydrazine, a compound is formed. Carbonic anhydride, alcohol, oxalic acid, and an aromatic compound were detected among the products of heating the oil with baryta in a sealed tube.
A. G. B.

**Sodium Glyoxylate.** By CARL BOETTINGER (*Arch. Pharm.*, 1896, **234**, 91).—*Sodium glyoxylate*, $NaC_2H_3O_4$, is precipitated when sodium ethoxide is added to an alcoholic solution of glyoxylic acid.
A. G. B.

**Derivatives of Glycollic acid.** By CARL BOETTINGER (*Arch. Pharm.*, 1896, **234**, 158—160),—*Orthoanisidine glycollate*, prepared by heating a mixture of glycollic acid and orthoanisidine in molecular proportion, crystallises in nearly colourless, six-sided tables, melts at 77—78°, and dissolves easily in cold water; strong nitric acid dissolves it to a dirty violet coloured solution.

*Glycollic orthoanisidide* is obtained by heating crystallised glycollic acid (1 part) with orthoanisidine (1½ part) at 150—160°; it crystallises in small, silvery laminæ, melts at 102—103°, and dissolves sparingly in water, but freely in hot ethylic and methylic alcohols.

*Paranisidine glycollate* crystallises in needles, melts at 85—86°, and dissolves easily in water and warm alcohol; it colours strong nitric acid blue, the colour quickly changing to violet, and becoming red on dilution.

*Glycollic paranisidide* crystallises in long, soft needles, melts at 97°, and is very slightly soluble in cold water, but easily in warm methylic alcohol; strong nitric acid dissolves it to a yellowish-red liquid, the colour quickly changing to yellow.

*Paraphenetidine glycollate* forms massive, transparent crystals, melts at 95—96°, and dissolves easily in cold water; in strong nitric acid it dissolves with a violet colour, passing into blue.

*Glycollic paraphenetidide* crystallises in long, white, soft, felted needles, melts at 159—160°, and dissolves in ethylic and methylic alcohols.
A. G. B.

**Stereoisomeric Thiodilactylic acids.** By JOHAN M. LOVÉN (*Ber.*, 1896, **29**, 1132—1136).—One inactive thiodilactylic acid, $S(CHMe{\cdot}COOH)_2$, has been previously described; it crystallises in monoclinic prisms, $a : b : c = 1{\cdot}4288 : 1 : 1{\cdot}0105$; $\beta = 75° 49' 45''$, melts at 125°, is soluble in 6·67 parts of water at 14°, and in all proportions at 100°. The sp. gr. of a saturated solution at 14° = 1·033; $K = 0{\cdot}049$. The amide crystallises in long, asbestos-like needles, melts at 18°, and dissolves in 19·46 parts of water. From the mother liquor of the acid, an isomeric inactive *acid* is deposited in needles; these, when further purified, change to prisms, probably belonging to the triclinic system; the separation of the acids is effected mechanically, or by fractional crystallisation from water. It melts at 109°, and dissolves in 2·438 parts of water at 14°. The sp. gr. of a saturated aqueous solution = 1·082 at 14°; $K = 0{\cdot}044$. The *amide* crystallises in short, transparent prisms, and is less soluble than the isomeric compound, dissolving in 47·08 parts of water at 18°. The acids differ from thiolactylhydracylic acid (compare following abstract), and are formed both from bromopropionic acid and from chloropropionic acid, they therefore appear to be stereoisomerides, but it is impossible to say which is the racemic and which the meso-form, as all attempts to resolve them into active components have been unsuccessful. J. B. T.

**Thiodihydracrylic acid and β-Sulphonedipropionic acid.** By JOHAN M. LOVÉN (*Ber.*, 1896, **29**, 1136—1139).—*Thiodihydracrylic* [*thiodipropionic*] *acid*, $S(CH_2{\cdot}CH_2{\cdot}COOH)_2$, is prepared by the interaction of sodium hydrogen sulphide and sodium β-iodopropionate in concentrated aqueous solution; it is also formed in small quantity in the preparation of thiohydracrylic acid; it crystallises from water in long, pearly, lustrous, rhombic plates, melts at 128°, and dissolves in 29·6 parts of water at 26·1°; $K = 0{\cdot}0078$. The salts are not characteristic. The *barium* salt forms nodular aggregates, but when the solution is quickly evaporated, it becomes gummy.

*β-Sulphonedipropionic acid*, $SO_2(CH_2{\cdot}CH_2{\cdot}COOH)_2$, is obtained by the oxidation of the preceding compound by means of potassium permanganate or bromine water; it crystallises in lustrous, hexagonal plates, melts at 210°, and dissolves in 441 parts of water at 26·8°; $K = 0{\cdot}024$. The *ethylic* salt crystallises in voluminous groups of slender, silky, lustrous needles, melts at 82·5°, and is readily soluble in hot, but not in cold, alcohol. It does not react with sodium ethoxide and ethylic iodide at 120°. Dithiodihydracrylic acid is soluble in about 1000 parts of water at the ordinary temperature.

J. B. T.

**Unsymmetrical Homologues of Thiodiglycollic acid and of Sulphonediacetic acid.** By JOHAN M. LOVÉN (*Ber.*, 1896, **29**, 1139—1143).—Unsymmetrical homologues of thiodiglycollic acid, corresponding with unsymmetrical ethers, are prepared by the interaction of the neutral sodium salts of mercapto-acids and those of haloïd fatty acids in concentrated aqueous solution. *Thioglycolhydracrylic* [*acetic-β-thiopropionic*] *acid*, $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}COOH$, is prepared from sodium thiohydracrylate and sodium chloracetate in presence of soda, and may also be obtained from sodium thioglycollate and sodium β-iodopropionate. Under these conditions the bivalent sulphur is not asymmetric. The acid is crystalline, stable in air, and melts at 94°; $K = 0{\cdot}025$. *Thiolactylglycollic* [*acetic-α-thiopropionic*] *acid*, $COOH{\cdot}CHMe{\cdot}S{\cdot}CH_2{\cdot}COOH$, prepared from sodium thiolactate and sodium chloracetate, is readily soluble, crystallises in plates, and melts at 87—88°; $K = 0{\cdot}048$. *Thiolactylhydracrylic* [*αβ-thiodipropionic*] *acid*, $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CHMe{\cdot}COOH$, from sodium thiolactate and sodium β-iodopropionate, is stable in air, and crystallises in prisms melting at 72—73°; $K = 0{\cdot}021$.

The above acids are readily oxidised to sulphone acids by means of potassium permanganate (2 per cent.). *Acetic-β-sulphonepropionic acid*, $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2{\cdot}COOH$, crystallises in lustrous plates, melts at 154—155°, and is stable in air; $K = 0{\cdot}51$. *Acetic-α-sulphonepropionic acid*, $COOH{\cdot}CHMe{\cdot}SO_2{\cdot}CH_2{\cdot}COOH$, crystallises in small plates, melting at 129°, and is readily soluble; $K = 1{\cdot}24$. *αβ-Sulphonedipropionic acid*, $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}CHMe{\cdot}COOH$, crystallises in spherical aggregates of microscopic needles, is readily soluble, stable in air, and melts at 131°. J. B. T.

**Stereoisomeric Dimethyldihydroxyadipic acids.** By NICOLAI D. ZELINSKY and W. ISAIEFF (*Ber.*, 1896, **29**, 819—820).—These acids, $C_2H_4[CMe(OH){\cdot}COOH]_2$, can be obtained in good yield by treating a mixture of acetonylacetone (1 mol.) and potassium cyanide (2 mols.) with strong hydrochloric acid (2 mols.) at 0°, and hydrolysing the product. The acid is added slowly, the mixture left for three days, then treated with an equal volume of strong, hydrochloric acid, and again allowed to remain; the hydrolysis of the dicyanhydrin then takes place at the ordinary temperature. The product was fractionally crystallised from water, and there were obtained (1) a less soluble acid, melting at 212°, with conductivity $K = 0{\cdot}0317$; and, in small quantity, (2) a more soluble acid, melting at 191—192°, and with conductivity $K = 0{\cdot}0330$, possibly itself a mixture of isomeric acids. C. F. B.

**Two Isomeric Ketodicarboxylic acids.** By WILLIAM O. EMERY (*J. pr. Chem.*, 1896, [2], **53**, 303—307).—*Acetonylsuccinic acid*, $COMe{\cdot}CH_2{\cdot}CH(COOH){\cdot}CH_2{\cdot}COOH$, is prepared by heating ethylic α-acetyltricarballylate (Abstr., 1891, 423) with twice its volume of hydrochloric acid (sp. gr. 1·11) in a reflux apparatus until no more carbonic anhydride is evolved, and evaporating the product on the water bath; it crystallises in laminæ, melts at 107°, and dissolves freely in water; the *silver* and *barium* salts were prepared. When the acid is heated at 200° under 12 mm. pressure, the *anhydride* distils over; it crystallises in small, white prisms, melts at 95°, and dissolves easily in chloroform, but only sparingly in carbon bisulphide; hot water converts it into the acid.

*β-Acetylglutaric anhydride*, $C_7H_8O_4$, is the product of treating ethylic β-acetyltricarballylate with hydrochloric acid in the manner described above; it crystallises in prisms, and melts at 102°. The author has not succeeded in converting the anhydride into the acid, but the *silver* and *barium* β-acetylglutarates have been prepared.

A. G. B.

**Action of Ethylic β-Bromolevulinate on Ethylic Sodiomalonate.** By WILLIAM O. EMERY (*J. pr. Chem.*, 1896, [2], **53**, 308—312).—Conrad and Guthzeit (Abstr., 1885, 42; 1886, 336) prepared the ethylic salt of an acid, which they termed α-carboxy-β-acetylglutaric acid, by the action of ethylic β-bromolevulinate on ethylic sodiomalonate; by heating this acid, they obtained one which melted at 109°, and was termed β-acetylglutaric acid. The author finds that the last-named acid really melts at 107°, and is acetonylsuccinic acid (preceding abstract), the immediate product of the action of ethylic β-bromolevulinate on ethylic sodiomalonate being *ethylic carboxyacetonylsuccinate*, $COMe\cdot CH_2\cdot CH(COOEt)\cdot CH(COOEt)_2$, which boils at 188—189° (11 mm.), has a sp. gr. = 1·1320 at 20°/4°, and is also formed by the interaction of ethylic acetylacrylate and ethylic sodiomalonate.

A. G. B.

**Action of Thiosinamine [Allylthiocarbamide] on Mercuric Iodide in presence of Ammonia.** By OTTO FOERSTER (*Chem. Zeit.*, 1895, **19**, 1895).—The author shows that by mixing an ammoniacal solution of allylthiocarbamide or of allylthiocarbimide with a solution of mercuric iodide in potassium iodide, an orange-yellow precipitate is obtained, which turns black slowly when exposed to light, or rapidly when treated with potassium cyanide. The yellow precipitate has the constitution $2HgS,HgI_2,NH_3$, and, when treated with potassium cyanide, leaves a black residue of mercuric sulphide.

J. J. S.

**Thiosinamine [Allylthiocarbamide] III.** By J. GADAMER (*Arch. Pharm.*, 1896, **234**, 1—47; compare this vol., i, 140).—Allylthiocarbamide dibromide, $C_4H_8N_2SBr_2$, melts at 139° (Falke gives 136—137°, Maly 146—147°); it is not converted into bromopropylenepseudothiocarbamide by recrystallisation. When its aqueous solution is treated with a deficiency of gold chloride, the aurobromide, $C_4H_8N_2SBr_2,AuBr_3$ is formed; but an excess of the chloride produces the aurochloride of the bromochloride,

$$C_4H_8N_2SBrCl,AuCl_3;$$

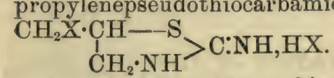
the fact that the second bromine atom remains under this treatment indicates that it is situated differently from the other bromine atom. The *picrate*, $C_4H_7N_2SBr,C_6H_3N_3O_7$, melts at 184—185°. Allylthiocarbamide bromochloride melts at 128·5°. No conclusion was arrived at concerning the nature of the product of the action of silver oxide on the dibromide. The diiodide, $C_4H_8N_2SI_2$, melts and decomposes at 130·5°; one atom of iodine can be precipitated from it by silver nitrate solution; the *picrate*, $C_4H_7N_2SI,C_6H_3N_3O_7$ melts at 178—179°. The chloriodide, $C_4H_7N_2SI,HCl$, was prepared by Maly; it melts at 132—133°; its *aurochloride* and *platinochloride* were prepared. By the prolonged action of excess of silver nitrate on the diiodide, and treatment of the filtrate with platinic chloride, a *platinochloride*, $(OH\cdot C_4H_7N_2S)_2,H_2PtCl_6$, was obtained, and an *aurochloride*, $OH\cdot C_4H_7N_2S,HAuCl_4$, was also prepared. Silver oxide converts the diiodide into the *base*, $C_4H_7IN_2S$. Allylthiocarbamide dichloride was not prepared in a pure condition by the action of chlorine on allylthiocarbamide, but the *platinochloride*,

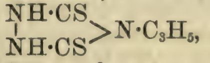
$$(C_4H_7N_2SCl)_2,H_2PtCl_6,$$

and the *picrate*, $C_4H_7N_2SCl,C_6H_3N_3O_7$ (m. p. 173—174°), are described.

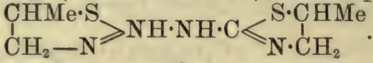
The author has confirmed Gabriel's observations on the conversion of allylthiocarbamide into β-methylethylenepseudothiocarbamide (propylenepseudothiocarbamide) by halogen hydrides, and finds that the change takes place in the cold.

Henry's bromallylthiocarbamide (m. p. 111°) was prepared, and attempts were made to convert it into the isomeric pseudothiocarbamide by Gabriel's method. Since no success attended these efforts, the author concludes that bromallylthiocarbamide is of the form $NH_2\cdot CS\cdot NH\cdot CH_2\cdot CBr{:}CH_2$, not $NH{:}CSH\cdot NH\cdot CH_2\cdot CBr{:}CH_2$.

The reduction of allylthiocarbamide bromide and iodide with various reducing agents led to no very definite results, nor did bromine water have the simple oxidising action on the bromide that it has on β-methylethylenepseudothiocarbamide; potassium chlorate and hydrochloric acid, however, oxidised the bromide to β-chlorobromomethyltaurocarbamic acid, a change which resembles the action of bromine water on β-methylethylenepseudothiocarbamide, and, in the author's opinion, warrants the conclusion that the allythiocarbamide haloïds are merely halogen substitution products of Gabriel's propylenepseudothiocarbamide, to be expressed by the formula  $\left.\begin{array}{l}CH_2X\cdot CH{-}{-}S\\ \;\;|\\ CH_2\cdot NH\end{array}\right>C{:}NH,HX$. Like the parent compound, allylthiocarbamide dibromide combines readily with methylic iodide (compare Beilstein, 1893, [3], i, 1321, 1324). A. G. B.

**Action of Hydrochloric acid on Hydrazodicarbothioallylamide.** By MARTIN FREUND and R. L. HEILBRUN (*Ber.*, 1896, **29**, 859—863).—When hydrazodicarbothioallylamide (Abstr., 1894, i, 97) is boiled with hydrochloric acid, three distinct products are obtained. *Allyldithiourazole*,  $\left.\begin{array}{l}NH\cdot CS\\ |\\ NH\cdot CS\end{array}\right>N\cdot C_3H_5$, is precipitated from the acid solution by the addition of water. It is dimorphous, crystallising in long needles and in large rhombohedral crystals, which melt at 136—137°. The *silver* salt, $C_5H_5N_3S_2Ag_2$, is a white, curdy precipitate. When it is treated with methylic iodide, or when the urazole is treated with sodium methoxide, and methylic iodide, *methylallylthiourazole*, $C_5H_6MeN_3S_2$, is formed; this melts at 68—70°, and has basic properties, yielding a *hydrochloride* which crystallises in silky needles and melts at 159—161°. The *diacetyl compound*, $C_5H_5Ac_2N_3S_2$, crystallises in yellow plates and melts at 94·5°. The *monacetyl derivative* melts at 176—177°, and dissolves in sodium carbonate solution. When allyldithiourazole is evaporated with hydrogen peroxide, a *compound* of the formula, $C_5H_5N_3S_2$, melting at 166—167°, is produced.

The acid filtrate from the allyldithiourazole contains 1-allyl-5-allylimido-2-thiourazole, which has been previously obtained by Freund and Wischewiansky (Abstr., 1894, 97), and *dipropylene-ψ-hydrazodicarbothiamide*,



$\begin{array}{l}CHMe\cdot S\\ \,|\\ CH_2—N\end{array}\!\!\geqslant NH\cdot NH\cdot C\leqslant\!\!\begin{array}{l}S\cdot CHMe\\ \;\;|\\ N\cdot CH_2\end{array}$. The latter is insoluble in water, forms slender needles, or compact crystals, and melts at 196—197°. The *hydrochloride* crystallises in needles, melting at 217°, and the *platinochloride* decomposes at about 240°. The *acetyl derivative*, $C_8H_{12}Ac_2N_4S_2$, melts at 242°, whilst the *dimethyl* derivative forms a syrupy mass. When the hydrochloride is treated with sodium nitrite, a *nitroso-compound*, $C_8H_{12}(NO)_2N_4S_2$, is formed which begins to decompose at 110°. A. H.

**Water of Crystallisation and Reactions of Alloxantin.** By C. HEINRICH L. RITTHAUSEN (*Ber.*, 1896, **29**, 892—893).—The formula of alloxantin is stated in some text-books, including Beilstein, to be $C_8H_4N_4O_7 + 3H_2O$, in others to be $C_8H_6N_4O_8 + 2H_2O$; the author has analysed two preparations of different origin and finds that the latter formula is correct. The compound becomes completely anhydrous after heating at 150° during 1—1½ hours, or at 107—110° for about five hours. A purple solution is obtained by heating alloxantin (1—2 milligrams) with a drop of nitric acid (sp. gr. = 1·4), constantly stirring until the acid is volatilized, and dissolving the residue in a little ammonia and water. Convicin reacts in a similar manner (compare following Abstr.).

J. B. T.

**Alloxantin as a Decomposition Product of Convicin from Sow-beans (Vicia faba minor) and Vetches (Vicia sativa).** By C. HEINRICH L. RITTHAUSEN (*Ber.*, 1896, **29**, 894—896).—A compound, apparently identical with convicin from vetch seed, crystallises from alcoholic extract of sow-beans, the yield is 60 grams from 150 kilos. of beans. When boiled for two minutes with dilute sulphuric acid (1 : 2), it slowly deposits alloxantin. The same result is obtained by dissolving convicin in concentrated hydrochloric acid, the yield being about 36 per cent. of the convicin employed. Convicin from vetch seed acts in a similar manner, its formula is $C_{10}H_{15}N_3O_7 + H_2O$, not $C_{10}H_{14}N_3O_7 + H_2O$, as previously stated; although identical with the compound from sow-beans in appearance and behaviour with acids, the latter appears to have the formula $C_{10}H_{15}N_3O_8,H_2O$. The alloxantin was identified by analysis, and by its various colour reactions. J. B. T.

**Deoxyfuroïn.** By RICHARD BADER (*Chem. Zeit.*, 1895, **19**, 1939).—Furoïn (Fischer, Abstr., 1882, 499), when reduced in alcoholic solution by means of tin foil and concentrated hydrochloric acid yields *deoxyfuroïn*. The reaction is carried out in the cold and is complete when a portion of the solution no longer gives a dark green colour if treated with caustic soda. The solution is filtered, gradually diluted with water, and extracted several times with ether; the combined ethereal extract is then washed 10—12 times with cold water and dried over calcium chloride, and the brownish syrup which is left on evaporating the ether is purified by distillation in steam. *Deoxyfuroïn* distils between 250° and 260° under a pressure of 755 mm., at the same time undergoing slight decomposition. The distillate on cooling sets to a mass of large, thick crystals which melt again at the ordinary temperature, and undergo decomposition when exposed to the air and bright sunlight. It is readily soluble in most organic solvents, slightly in hot water and readily in cold sodium hydroxide solution. No oxime or hydrazone could be obtained.

Benzofuroïn, when reduced in a similar manner, yields *deoxybenzofuroïn* in small quantities. J. J. S.

**Furfuraldehyde and Carbonic Anhydride from Glycuronic acid.** By F. MANN and BERNHARD TOLLENS (*Annalen*, 1896, **290**, 155—158).—Glycuronic acid is prepared from Purree, or Indian yellow, by digesting it with dilute hydrochloric acid, submitting it to pressure, and hydrolysing with 10 per cent. sulphuric acid the euxanthic acid extracted from the residue; the specific rotatory power of glycuronic anhydride is $[\alpha]_D = +18{\cdot}2°$.

It having been shown that glycuronic anhydride yields furfuraldehyde on distillation with hydrochloric acid (Abstr., 1892, 1433), the authors have attempted to express the action quantitatively; from 1 gram of the anhydride, 15 per cent. of furfuraldehyde, and 26·5 per cent. of carbonic anhydride have been obtained, the equation $C_6H_8O_6 = C_5H_4O_2 + 2H_2O + CO_2$ requiring 54 per cent. and 25 per cent. respectively.

Furfuraldehyde has been also obtained from euxanthic, urochloralic, and urobutylchloralic acids. M. O. F.

**Preparation of Siliconchloroform, Siliconbromoform, and Triphenylsiliconprotane.** By CHARLES COMBES (*Compt. rend.*, 1896, **122**, 531—533).—On passing dry hydrogen chloride over copper silicide, heated in a vapour bath of either sulphur, mercury, or diphenylamine, siliconchloroform is produced in quantities of about 80 per cent. of the theoretical yield, the remaining 20 per cent. consisting chiefly of the tetrachloride, from which it can be readily separated by fractionation.

With hydrogen bromide, a somewhat smaller quantity of the corresponding bromo-derivative is produced, owing to partial dissociation of the halogen acid, with formation of copper bromide.

With hydrogen iodide, no siliconiodoform is produced.

On mixing dry ethereal solutions of aniline and siliconchloroform, a crystalline substance, $SiHCl(NHPh)_2$, separates on concentration; when excess of aniline is employed, the compound $SiH(NHPh)_3$ is produced. The latter, when treated with dry hydrogen chloride, is converted into aniline hydrochloride and siliconchloroform, thus showing that nitrogen intervenes between the silicon and the phenyl group. J. F. T.

**Derivatives of Triphenylsiliconprotane.** By Charles Combes (*Compt. rend.*, 1896, **122**, 622—624; compare preceding abstract).—By the action of sodium on a dry ethereal solution of molecular proportions of silicon tetrachloride and parabromodimethylaniline a voluminous crystalline mass is produced of the formula

$$SiH(C_6H_4{\cdot}NMe_2)_4.$$

This, on recrystallisation from hot light petroleum, forms slender, needle-shaped crystals, melting and decomposing at 225°.

By operating in the same way with siliconchloroform, the compound $SiH(C_6H_4{\cdot}NMe_2)_3$ is produced; it crystallises from acetone in small prisms, and melts at 152°.

On oxidation, these substances readily produce colouring matters. They are, however, the same as those produced by the oxidation of dimethylaniline and do not contain silicon.

$OH{\cdot}Si(C_6H_4{\cdot}NMe_2)_3$ is produced by the action of mercuric nitrate on the triphenyl derivative, it melts at 188—189°, and is soluble in all the usual solvents. J. F. T.

**Formation of 1 : 2 : 3-Trimethylbenzene together with Synthetical Mesitylene.** By Ad. Lucas (*Ber.*, 1896, **29**, 953—958; compare Abstr., 1895, i, 356).—Acetone purified by means of sodium hydrogen sulphite is converted by the action of sulphuric acid, into mesitylene, which is purified by repeated fractionation over sodium; the portion boiling at 160—170° yields with acetic chloride, mesityl methyl ketone, and this, when oxidised, gives mesitylglyoxalic acid, $C_6H_2Me_3{\cdot}CO{\cdot}COOH$, which is then distilled. Unchanged mesitylglyoxalic acid is removed from the distillate by treating it with water at 30° (Claus' statement as to its insolubility being incorrect), and the remaining acid is then etherified by V. Meyer's method; in this manner, the three trimethylbenzoic acids, 1 : 2 : 4 : 6-, 1 : 2 : 3 : 4-, and 1 : 3 : 4 : 5-, [COOH = 1], are formed, the last in smallest quantity. No isomeric acid derived from 1 : 2 : 4-trimethylbenzene (pseudocumene) could be detected. The trimethylbenzaldehye, which is also formed by the distillation of the glyoxalic acid, yields, in addition to mesitylantialdoxime (m. p. 124—125°), a synaldoxime melting at 168°, and an antialdoxime which crystallises in lustrous prisms melting at 115°; both are probably derived from the aldehyde [CHO : $Me_3$ = 1 : 2 : 3 : 4]. No 1 : 2 : 4-trimethylbenzene derivatives could be detected. About 10 per cent. of the original trimethylbenzene consisted of the 1 : 2 : 3-compound, and the remainder of mesitylene. The higher fractions obtained in the original distillation after the separation of the trimethylbenzenes, are readily oxidised by potassium permanganate, and do not consist of benzene derivatives. Attempts were made to prepare trimethylbenzene by passing methylacetylene through heated tubes containing pumice; in spite of varying the temperature, only carbonaceous matter could be obtained; under similar circumstances, acetylene yields comparatively little benzene, but more highly condensed compounds, carbonaceous matter also is produced in considerable quantity (compare following abstract).

J. B. T.

**Synthesis and Constitution of Benzene.** By ARTHUR R. HANTZSCH (*Ber.*, 1896, **29**, 958—960).—The direct condensation of acetone to trimethylbenzene can only yield the symmetrical compound, but if, as Fittig has suggested, methylacetylene is first formed, and the group CH combines with only one additional carbon atom (peripheral linkage) the trimethyl compounds 1 : 3 : 5- and 1 : 3 : 4- should be produced. The investigations of Lucas (preceding abstract) show that the latter compound is not formed at all, the condensation products being only 1 : 3 : 5- and 1 : 2 : 3-, the latter in smaller proportion. This suggests that each carbon atom actually combines with two others (centric linkage), which fully accords with the facts. A combined peripheral and centric linkage should give rise to all three trimethylbenzenes, and, therefore, need not be considered. Von Baeyer's observations on the stability of the para-linkage in reduced benzene derivatives thus receive support from a synthetical standpoint.

J. B. T.

**Formation of Salts from Trinitrobenzene.** By VICTOR MEYER (*Ber.*, 1896, **29**, 848—850).—The author considers that the coloured solutions which polynitro-compounds give with alkalis contain salts formed by the replacement of hydrogen in the benzene nucleus. Lobry de Bruyn, on the other hand, supports the view that the formation of these coloured solutions is accompanied by a decomposition which results in the formation of nitrous acid. When pure trinitrobenzene, however, is treated with pure soda, which produces a red coloration, and pure sulphuric acid is immediately added, no nitrous acid can be detected in the liquid. Precisely similar results are obtained with pure trinitrobenzoic acid. Dinitrothiophen, moreover, yields a reddish-brown silver salt which is decomposed by hydrochloric acid with regeneration of the pure dinitro-compound. Lobry de Bruyn's salt, $C_6H_3(NO_2)_3 + KOCH_3 + \frac{1}{2}H_2O$, probably has the constitution $C_6H_2K(NO_2)_3 + CH_3{\cdot}OH + \frac{1}{2}H_2O$.

A. H.

**New Synthesis of some Aromatic Nitriles.** By ALEXANDRE DESGREZ (*Bull. Soc. Chim.*, 1895, [3], **13**, 735—737).—Under suitable conditions, cyanogen may be made to act as a halogen, and directly displace hydrogen in such hydrocarbons as benzene, toluene, the two xylenes, and mesitylene; the yield is about 12 per cent. of the theoretical.

The method employed is to conduct the cyanogen gas into the hydrocarbon (boiling under a slight pressure) in the presence of aluminium chloride. By this means, the author has synthesised benzonitrile, which he has characterised by the formation of ethylic benzoate, benzamide, and benzoic acid.

In the formation of cyanogen from mercuric cyanide, the action is sensibly accelerated by the presence of a small quantity of mercuric chloride. J. F. T.

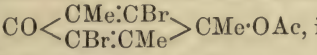
**Mandelonitrile.** By Ernst S. C. von Meyer (*J. pr. Chem.*, 1896, [2], **53**, 344).—With the intention of preparing amidobenzylic cyanide, mandelonitrile was left in contact with the calculated proportion of alcoholic ammonia, and gradually evaporated; small crystals of the formula, $C_{15}H_{12}N_2$, were obtained. The substance is being investigated, and this publication is made in view of E. Fischer's paper on the formation of oxazoles (this vol., i, 262). A. G. B.

**Distillation of Orthocresol with Lead Oxide.** By Berthold Jeiteles (*Monatsh.*, 1896, **17**, 57—64).—Orthocresol, with about twice its weight of lead oxide, is heated for some time in a reflux apparatus, and then distilled; the distillate, when shaken with strong caustic potash, leaves undissolved a reddish *substance*, which is crystallised from alcohol, thereby becoming pale yellow. On sublimation, it condenses in long, white needles which begin to sublime at 150° and melt at 162—163°. When treated with sulphuric acid, the substance gives the greenish-blue fluorescence characteristic of xanthones. On reduction with hydriodic acid, it yields a *substance* which is volatile in steam, crystallises from alcohol in white scales, melts at 93°, and gives the xanthone reaction with sulphuric acid. This compound is attacked by alcoholic potash, yielding a phenolic *substance* which dissolves readily in alcohol, and, with phenylhydrazine, gives an ill-defined *compound* containing nitrogen. When fused with potash, it is decomposed with production of a phenol which gives a slight precipitate with bromine water, and an acid, volatile in steam, which crystallises in white needles, and shows the salicylic acid reaction with ferric chloride.

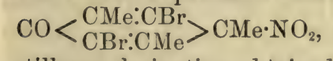
The author is of opinion, although the evidence is inconclusive, that he was probably dealing with a monomethylxanthone. A. L.

**Dibromopseudocumenol Bromide and analogous Compounds.** By Karl Auwers (*Ber.*, 1896, **29**, 1095—1110; compare this vol., i, 149).—It has been already shown that bases act on dibromopseudocumenol bromide with great readiness, and its behaviour towards aniline, piperidine, dimethylaniline, and pyridine has been studied (*loc. cit.*).

Ammonia gives rise to two products, $C_9H_9Br_2O{\cdot}NH_2$, and $(C_9H_9Br_2O)_3N$, according to the experimental conditions, whilst the action of aliphatic monamines leads to the formation of tertiary ammonium compounds. Although quinoline and tertiary bases generally yield additive compounds, aqueous trimethylamine is without action, and the solution in benzene loses hydrogen bromide, yielding a compound which does not dissolve in alkalis, and is probably identical with the substance obtained by decomposing the pyridine derivative, or by allowing the original bromide to remain in contact with aqueous soda.

The active bromine atom of dibromopseudocumenol bromide has been replaced by chlorine and iodine, and the compounds thus produced closely resemble the original bromide; the acetate of dibromohydroxypseudocumenol (this vol., i, 151), which melts at 113°, forms the intermediate compound in the production of these substances, and from this circumstance is drawn the conclusion that the bromide, chloride, iodide, and acetate are analogous in structure, and, as the constitution of the last-named is most plausibly represented by the formula  $\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{CMe{:}CBr}}{\mathrm{CBr{:}CMe}}>\mathrm{CMe{\cdot}OAc}$, it follows that Zincke's interpretation of the structure of dibromopseudocumenol bromide (this vol., i, 214) is correct. The experimental matter on which this deduction depends is dealt with in the following abstracts.

The author has already described a remarkable nitro-compound obtained by the action of fuming nitric acid on pseudocumenol (Abstr., 1885, 380) having the formula $C_9H_{10}N_2O_5$; it melts at 81·5° (not at 84°), and, although insoluble in alkali, is readily converted by alcoholic ammonia into the true dinitropseudocumenol, with which it is isomeric, and easily loses a nitro-group, passing into nitropseudocumenol. Whilst recent investigation has shown that the last-named is orthonitropseudocumenol, and not the meta-compound, the position of the second nitro-group has not been determined. Owing to the readiness with which yellow ammonium sulphide eliminates the nitro-group, the compound in question forms a convenient source of orthonitropseudocumenol, which cannot be obtained by direct nitration of the phenol.

An analogous *nitro-compound* of dibromopseudocumenol is obtained by the action of cold, fuming nitric acid; it has the formula $C_9H_9Br_2NO_3$, melts at 102—103°, and crystallises from a mixture of ether and petroleum in splendid plates. The isomeric *dibromopseudocumenol nitrite* is obtained by the action of silver nitrite on dibromopseudocumenol bromide dissolved in benzene; it crystallises from petroleum in yellowish, lustrous plates, and melts, evolving gas, at 135°. It is probable that this compound has the constitution  $\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{CMe{:}CBr}}{\mathrm{CBr{:}CMe}}>\mathrm{CMe{\cdot}NO_2}$, as hot dilute alkali converts it into the stilbene derivative obtained under similar conditions from dibromopseudocumenol bromide, nitrous acid being eliminated.

When pseudocumenol is chlorinated by Reimer's method, a product is obtained which melts at 96·5° (not at 98°), and has the empirical formula $C_{10}H_{12}Cl_2O$. It is indifferent towards aniline, phenylhydrazine, and phenylic cyanate, and undergoes no change when heated with a mixture of fuming nitric and concentrated sulphuric acids. According to the experimental conditions, bromine gives rise to two *compounds*, $C_{10}H_{10}Cl_2Br_2O$, which crystallises from glacial acetic acid in long needles, and melts at 147°, and $C_{10}H_9Cl_2Br_3O$, which is obtained in lustrous leaflets, and melts at 203—204°. M. O. F.

**Dibromopseudocumenol Bromide, Chloride, and Iodide.** By KARL AUWERS and L. HOF (*Ber.*, 1896, **29**, 1110—1120; compare the foregoing abstract).—When dibromopseudocumenol bromide in benzene solution is agitated with concentrated aqueous ammonia, the *compound* $N(CH_2{\cdot}C_6Me_2Br_2{\cdot}OH)_3$ is produced; it crystallises from xylene in short needles, and melts between 218° and 224°, according to the rate at which the temperature rises. The substance dissolves readily in ether, being more sparingly soluble in alcohol and benzene, and almost insoluble in chloroform and petroleum; it is indifferent towards hot alkalis, and is converted by glacial acetic acid into tetrabromodihydroxytetramethylstilbene (this vol., i, 150). The *hydrobromide* melts and decomposes at 236°; the *ethyl ether* crystallises from glacial acetic acid in lustrous prisms, and melts at 196—197°.

If gaseous ammonia is passed into a benzene solution of dibromopseudocumenol bromide during several hours, the filtered liquid deposits the *compound* $NH_2{\cdot}CH_2{\cdot}C_6Me_2Br_2{\cdot}OH$, which separates from a mixture of chloroform and petroleum in white, prismatic crystals, and melts at 106°; it dissolves readily in ether, choroform, and benzene; with difficulty, however, in petroleum. The *hydrobromide* crystallises from glacial acetic acid in needles, and melts at 159—161°, the solvent converting it into the stilbene compound already mentioned. On adding water to the solution of the amine in acetic acid, the acetate of dibromopseudocumenol, which melts at 115°, is produced.

When aqueous methylamine is added to dibromopseudocumenol bromide dissolved in benzene, the *methylamine derivative*,

$$NMe(CH_2{\cdot}C_6Me_2Br_2{\cdot}OH)_2,$$

is produced; it crystallises from chloroform in needles, and melts at 173° when rapidly heated. It undergoes no change when heated alone on the water bath, but boiling caustic soda converts it into the stilbene derivative. The *hydrobromide* crystallises from chloroform, and melts at 195°; the *phenylurethane derivative* crystallises from a mixture of chloroform and petroleum in white prisms, and melts at 202°.

The *ethylamine derivative* of dibromopseudocumenol bromide, $NEt(CH_2{\cdot}C_6Me_2Br_2{\cdot}OH)_2$, crystallises from chloroform and petroleum in rhombic prisms, and melts at 165·5°; the *hydrobromide* separates from glacial acetic acid in needles, sinters at 130°, and melts, decomposing, at 218°. The *diethylamine derivative* of dibromopseudocumenol bromide, $NEt_2{\cdot}CH_2{\cdot}C_6Me_2Br_2{\cdot}OH$, melts at 87°; the *hydrobromide* crystallises from chloroform in needles, and melts at 182°.

As already stated (foregoing abstract), aqueous trimethylamine is without action on dibromopseudocumenol bromide; the solution in benzene, however, eliminates hydrogen bromide, and converts it into the *compound* $C_{18}H_{16}Br_4O_2$, which is insoluble in alkalis, crystallising from aniline, naphthalene, and nitrobenzene in dark brown needles which melt at 230°, and evolve gas at 250°. The same product is formed under the influence of 10 per cent. aqueous caustic soda, the stilbene derivative also being formed. Moist silver oxide, however, converts dibromopseudocumenol bromide into an amorphous *compound*, $C_9H_{10}Br_2O_2$, which melts at 240—245°.

Tetrabromodihydroxytetramethylstilbene *bromide*,

$$C_2H_2Br_2(C_6Me_2Br_2{\cdot}OH)_2,$$

is obtained by adding bromine to the stilbene derivative already mentioned; it crystallises from glacial acetic acid and petroleum, and melts at 179°.

*Dibromopseudocumenol iodide*, $C_6Me_3Br_2{\cdot}OI$, is obtained by the action of hydriodic acid on the acetate of dibromopseudocumenol, and crystallises from glacial acetic acid in white needles which melt at 134—136°; it closely resembles the bromide in properties, and is converted by boiling methylic alcohol into dibromomethoxypseudocumenol.

*Dibromopseudocumenol chloride*, $C_6Me_3Br_2{\cdot}OCl$, is produced when hydrogen chloride acts on the acetate, and crystallises from glacial acetic acid or petroleum in needles melting at 109—110°.

During the preparation of dibromopseudocumenol bromide, in addition to the stilbene derivative, there are formed two bye-products, the *compound* $C_{11}H_{13}Br_2O$, which crystallises in white needles and melts at 174°, and the *compound* $C_9H_9Br_3O$, isomeric with dibromopseudocumenol bromide, which crystallises from glacial acetic acid in white needles and melts at 181°. M. O. F.

**Products obtained from Dibromopseudocumenol Bromide by the Action of Aromatic Bases.** By KARL AUWERS and H. A. SENTER (*Ber.*, 1896, **29**, 1120—1128; compare the foregoing abtracts).—The *β-naphthylamine derivative*,

$$C_{10}H_7{\cdot}NH{\cdot}CH_2{\cdot}C_6Me_2Br_2{\cdot}OH,$$

is obtained by the action of β-naphthylamine on dibromopseudocumenol bromide dissolved in benzene, the stilbene derivative being formed at the same time; it crystallises from benzene in silvery leaflets, and melts at 181—182°. The substance is insoluble in water, ether, and petroleum, and is decomposed by hot glacial acetic acid, yielding the stilbene derivative; dilute soda is without action on the compound, and dissolves it slowly.

The *methylaniline derivative*, $OH{\cdot}C_6Me_2Br_2{\cdot}CH_2{\cdot}NMePh$, is prepared by adding dilute hydrochloric acid to a mixture of dibromopseudocumenol bromide and methylaniline, the *hydrochloride* thus obtained being then decomposed with soda; it crystallises from alcohol and petroleum in small, white needles, and melts at 99°. The *hydrobromide* loses hydrogen bromide at 60°.

The *quinoline additive-compound*, $C_9H_9Br_3O,C_9H_7N$, is insoluble in benzene, xylene, petroleum, acetone, and ethylic acetate, but crystallises from glacial acetic acid containing hydrogen bromide, and melts at 226°; if water is added to the solvent, dibromopseudocumenol acetate is produced.

The *diethylaniline derivative*, $OH{\cdot}C_6Me_2Br_2{\cdot}CH{:}NEt_2Ph$, crystallises from alcohol in long, slender needles, and melts at 89—90°; it is obtained by the action of boiling 10 per cent. soda on the *diethylaniline additive-compound*, which crystallises from glacial acetic acid in long, transparent needles melting at 256—257°.

The *methiodide* of the dimethylaniline derivative (this vol., i, 150) is obtained by heating the substance in benzene solution with methylic iodide at 100°; it crystallises in yellowish, lustrous leaflets, and melts and decomposes at 190—191°. The *ethobromide* crystallises in slender, pale brown needles, which melt and evolve gas at 189—192°; caustic soda converts it into a crystalline substance which melts at 153—154°. When the methiodide is treated with dilute aqueous soda, hydrogen iodide is eliminated, and the *base* $C_{18}H_{23}Br_2NO_2$ is produced, being also formed by the action of moist silver oxide on the methiodide; it is strongly alkaline towards litmus, and when crystallised from water melts at 205—207°.

The *methiodide* of the diethylaniline derivative melts at 177—178°, and is converted by soda into a *base*, which crystallises from hot water in lustrous needles, and melts at 191—192°.

The *hydriodide* of the aniline derivative is obtained by heating it with methylic iodide in benzene solution; it crystallises in needles, and melts at 182°. The *hydriodide* of the piperidine compound is prepared in the same manner, and crystallises in short prisms, melting at 206°. M. O. F.

**Bromo-derivatives of Asymmetrical Metaxylenol.** By KARL AUWERS and G. VON CAMPENHAUSEN (*Ber.*, 1896, **29**, 1129—1132; compare the foregoing abstracts).—When bromine acts on asymmetrical metaxylenol during a short period, Jacobsen's tribromoxylenol (m. p. 179°) is the sole product; if the action, however, is protracted, the main product consists of tribromoxylenol bromide, along with the dibromide, which does not dissolve in petroleum.

*Tribromoxylenol bromide*, $C_6Me_2Br_3{\cdot}OBr$, crystallises from petroleum in long, lustrous needles, and melts at 135—136°; boiling methylic alcohol converts it into *tribromomethoxyxylenol*,

$$OH{\cdot}C_6MeBr_3{\cdot}CH_2{\cdot}OMe,$$

which crystallises from petroleum in slender, white needles, and melts at 100°. *Tribromethoxyxylenol* melts at 110—112°.

*Tribromoxylenol dibromide*, $OH{\cdot}C_6Me_2Br_3,Br_2$, crystallises from glacial acetic acid in lustrous, white needles, and melts at 169—171°; boiling methylic alcohol converts it into *tribromodimethoxyxylenol*, which crystallises from petroleum in slender needles, and melts at 93—95°. *Tribromodiethoxyxylenol* melts at 62—64°. M. O. F.

**Derivatives of Eugenol.** By CH. GASSMANN (*Compt. rend.*, 1896, **122**, 395—397).—*Eugenolacetic acid*,

$$CH_2{:}CH{\cdot}CH_2{\cdot}C_6H_3(OMe){\cdot}O{\cdot}CH_2{\cdot}COOH\ [= 1:3:4],$$

is obtained by boiling eugenol with sodium hydroxide and chloracetic acid, precipitating with hydrochloric acid, and recrystallising from water at 70°. It melts at 75°, and dissolves in hot water, and most organic solvents. The salts are not decomposed by carbonic anhydride, and the sodium salt is precipitated from its aqueous solution by sodium chloride.

*Isoeugenolacetic acid*, $CHMe{:}CH{\cdot}C_6H_3(OMe){\cdot}O{\cdot}CH_2{\cdot}COOH$, is obtained by boiling eugenolacetic acid with a solution of potassium hydroxide. It is essential to a good yield that precipitation with hydrochloric acid should take place between 0° and 5°. Another method is to heat eugenolacetic acid with 2·5 times its weight of potassium hydroxide and five times its weight of water at 150° for 10 hours, or at 200° for half an hour, and a third method is to heat isoeugenol with sodium hydroxide and chloracetic acid. Isoeugenolacetic acid crystallises in white needles, which melt at 92—94°, and dissolve in most organic solvents. Its salts are less soluble than those of eugenolacetic acid, and are precipitated from their aqueous solutions by sodium hydroxide.

*Vanillinacetic acid*, $CHO{\cdot}C_6H_3(OMe){\cdot}O{\cdot}CH_2{\cdot}COOH\ [=1:3:4]$, is obtained by oxidising an alkali salt of isoeugenolacetic acid with potassium permanganate in presence of acetic or carbonic acid. It crystallises from alcohol in colourless crystals which melt at 188—190°, and is identical with the acid obtained from vanillin by the action of chloracetic acid in presence of an alkali. When treated with phosphorus pentachloride, it yields vanillin. C. H. B.

**Derivatives of Cholesterol.** By JULIUS MAUTHNER and WILHELM SUIDA (*Monatsh.*, 1896, **17**, 29—49; compare Abstr., 1894, i, 326, 486).—Of the three cholesterylenes described by Zwenger, and assigned by him the formula $C_{27}H_{42}$, *a*-cholesterylene has a molecular weight in naphthalene considerably greater than that corresponding with the above formula, whilst *b*-cholesterylene under the same conditions gives numbers agreeing with a molecular weight twice as great as that assigned to it by its discoverer. *a*-Cholesterylene, contrary to Zwenger's statements, does not melt at 240°, but sinters and turns yellow at 210—220°, becomes transparent at 235°, and liquefies finally at about 260°.

*a*-Cholesterone and *b*-cholesterone melted, not at 68° and 175°, but at 79·5—80·5° and 192° respectively. The latter compound is identical in properties with Walitzky's cholesterylene (compare this Journal, 1877, i, 58), and may be advantageously prepared in the following manner. Equal weights of anhydrous cholesterol and copper sulphate are mixed and heated at 200°; when cool, the product is extracted with benzene, the filtered solution evaporated, and the residue heated with alcohol; cholesterylic ether is left undissolved, whilst the cholesterylene dissolves and separates on cooling in large needles, whose geometrical and optical properties point to monosymmetric or orthorhombic symmetry respectively; in the former case, the geometrical constants are $a : b : c = 1{\cdot}1341 : 1 : ?$, $\beta = 131° 59' 40''$, and in the latter, $a : b : c = 0{\cdot}8359 : 1 : 0{\cdot}7525$. The substance is oxidised very slowly by alkaline permanganate, although its behaviour towards bromine and iodine demonstrates the presence of one ethylic union in the molecule. The *cholesterylic ether*, $(C_{27}H_{43})_2O$, is also formed on heating a mixture of cholesterylic chloride and zinc dust or zinc oxide at 200°, and appears as a bye-product in the preparation of cholesterylic chloride; it crystallises from a mixture of benzene and alcohol in attenuated, felted needles, sinters at 188°, and melts at about 195°; it is insoluble in alcohol, dissolves sparingly in ether, and readily in benzene and chloroform, its molecular weight in the last substance being normal; the crystals break up in sulphuric acid without producing fluorescence, the liquid on being warmed assuming a reddish-orange colour. By the action of bromine, the substance yields a *tetrabromide*, $(C_{27}H_{43}Br_2)_2O$, which crystallises in slender needles, and melts with disengagement of gas at 164—166°.

Cholesterylic chloride, when heated above its melting point, evolves hydrogen chloride, and at 150° a colourless, limpid liquid passes over; whilst at 345—390° a yellow oil with a violet fluorescence distils, leaving a deep brown, gummy residue. The portion of low boiling point redistils for the most part at 110—130°; its molecular weight combined with its behaviour towards bromine prove it to be a mixture of a paraffin and an olefine, probably octane and octylene. The portion of higher boiling point shows the cholesterol and cholestol reactions, combines with bromine, and has the composition $C_{19}H_{28}$.

Walitzky's cholesterylene, on distillation, yields a mixture of liquids which boil at 240—270°, 360—390°, and 400—410°; the last two probably have the formulæ $C_{16}H_{24}$ and $C_{20}H_{30}$ respectively.

By the action of silver nitrate on cholesterylic chloride in alcoholic solution, a *substance* of uncertain composition is obtained. It contains nitrogen, but no chlorine, crystallises from ethylic or methylic alcohol in beautiful, long crystals, melts at 81—82°, and, during solidification, the fused substance shows a magnificent play of colours. If in the preparation of this substance the solution be kept neutral by means of carbonic anhydride, no crystals are obtained, but if the product be extracted with ether, the solution evaporated, and the residual oil heated with nitric acid, the above substance crystallises out.

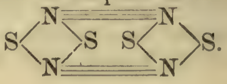
Nitrocholesterylic chloride has the normal molecular weight in naphthalene.

The authors mention that by the oxidation of cholesterol they have obtained a semi-crystalline substance, which yields a ketone whose hydrazone crystallises in beautiful golden-yellow needles. A. L.

**Veratrylamine.** By CHARLES MOUREU (*Compt. rend.*, 1896, **122**, 477—479).—*Veratrylamine*, $NH_2 \cdot C_6H_3(OMe)_2$ [= 1 : 3 : 4], is obtained by the reduction of nitroveratrol, $NO_2 \cdot C_6H_3(OMe)_2$. It crystallises from ether in brilliant, pale grey plates with a violet tinge, melts at 85—86°, and boils at 174—176° under a pressure of 22 mm. When freshly distilled, it is quite white, but gradually alters and becomes darker in colour when exposed to the air. The platinochloride melts and decomposes at 220°. *Benzoveratrylamine* forms slender, white needles which melt at 177°.

When diazotised in presence of hydrobromic acid and finely divided copper, veratrylamine yields *bromoveratrol*, an oily liquid, which boils at 250—254°, but distils easily with water. When diazotised in presence of cuprous cyanide, it yields a cyano-derivative which is identical with the nitrile obtained by Garelli's reaction, and yields veratric acid when hydrolysed. It follows that in veratrylamine [$NH_2$ : OMe : OMe = 1 : 3 : 4]. C. H. B.

**Sulphur Nitride.** By RUDOLF SCHENCK (*Annalen*, 1896, **290**, 171—185). The author discusses the properties of sulphur nitride, $N_4S_4$, and regards it as having the constitution



Sulphur nitride is obtained by passing dry ammonia gas into a solution of sulphur dichloride in benzene; it crystallises from carbon bisulphide in orange needles, melting at 178°, and not at 160°, as stated by previous investigators. The highly explosive character of the substance renders it advisable to preserve it in cardboard boxes instead of glass bottles. On adding it to a solution of sodium ethoxide (4 mols.) in alcohol, the liquid acquires a colour which is purple-red by transmitted, and dark green by reflected light, gradually becoming violet and ultimately brown; this coloration is permanent in absence of water, but if water is added the solution becomes yellow and acquires a most offensive odour. Absolute ether precipitates from the alcoholic solution a substance which crystallises in lustrous scales, and exhibits dichroism; it is excessively unstable, and the solution in alcohol is red.

Sulphur nitride is indifferent towards primary and secondary bases of the aromatic series and all tertiary bases. If the substance is covered with piperidine, heat is generated, ammonia and nitrogen being evolved, whilst the mass, on cooling, deposits thiopiperidine (Abstr., 1895, i, 430); the action proceeds quantitatively in accordance with the equation $3N_4S_4 + 24C_5H_{10}NH = 12(C_5H_{10}N)_2S + 8NH_3 + 2N_2$.

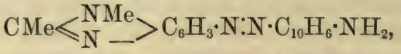
When sulphur nitride is heated for one hour with dimethylamine, and the product distilled, the fraction which boils below 100° is a colourless oil, which solidifies in a mixture of ice and salt; this substance is thiodimethylamine, crystallising in lustrous leaflets having a disagreeable, irritating odour. Ethylamine acts on sulphur nitride, producing tetrethylthiodiamine, $S(NEt_2)_2$ (Abstr., 1895, i, 264).

Sulphur nitride converts benzylamine into polymerised benzonitrile, the cyaphenine of Pinner and Klein (*Ber.*, **11**, 6), ammonia and nitrogen being evolved; when, however, the generation of heat is checked, and excess of benzylamine is employed, the *thionamide* of thiobenzoic acid, $S{:}CPh{\cdot}N{:}S$, is produced, crystallising from ethylic acetate in beautiful yellow prisms, melting at 104—105°. Along with this, a liquid is formed which becomes deep red when exposed for some days to air; on acidification, ether extracts the colouring matter, which consists of dithiobenzoic acid.

Cold phenylhydrazine is without action on sulphur nitride, but on application of heat, there is a violent disengagement of ammonia and nitrogen, benzene, sulphur, and hydrogen sulphide being also produced. M. O. F.

**Derivatives of *α*-Diamidodimethylaniline.** By A. SCHUSTER and JOHANNES PINNOW (*Ber.*, 1896, **29**, 1053—1057; compare Abstr., 1894, i, 281).—*β*-Dinitrodimethylaniline is best prepared by the action of 30 per cent. nitric acid on dimethylaniline dissolved in dilute sulphuric acid, and yields diamidodimethylaniline on reduction. When the base is boiled with acetic anhydride, methylethenylacetamidophenylenamidine is formed, along with diacetdiamidodimethylaniline, which melts at 151·5—152·5° (uncorr.), and crystallises from water with $1\frac{1}{2}H_2O$ (compare Wurster and Sendtner, *Ber.*, **12**, 1806). Methylethenylamidophenylenamidine melts at

167—168° (uncorr., compare Abstr., 1894, i, 281). The *picrate* melts at 248° (uncorr.). The solution of the corresponding diazo-compound can be boiled without undergoing decomposition. With β-naphthylamine, the diazo-salt yields a *colouring matter*,



$$\mathrm{CMe}{<}\begin{matrix}\mathrm{NMe}\\ \mathrm{N}\ \text{—}\end{matrix}{>}\mathrm{C_6H_3{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH_2},$$

which crystallises from aniline in orange-coloured needles, and melts and decomposes at 260° (uncorr.). This colouring matter is taken up by unmordanted cotton.

*Methylethenylnitroacetamidophenylenamidine* is formed by the nitration of the acetyl compound in presence of concentrated sulphuric acid. It crystallises from acetic acid in compact needles containing 1 mol. of the solvent, and melts, after drying, at 220—221° (uncorr.).

*Methylethenylnitramidophenylenamidine* crystallises in red needles, melting at 251—252° (uncorr.). When reduced, it yields *methyldiethenyltetramidobenzene*, which crystallises from water in needles; these contain $1H_2O$, and, after drying, do not melt below 260°. The *double salt* of the hydrochloride of this base with mercuric chloride forms lanceolate needles melting at 211—212° (uncorr.). A. H.

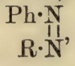
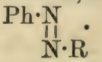
**Normal Diazo-metallic Salts.** By ARTHUR R. HANTZSCH and DIMITER GERILOWSKI (*Ber.*, 1896, **29**, 1059—1066).—In reply to the criticism of Bamberger (this vol., i, 362), the authors maintain the accuracy of their statements as to the relative rates of decomposition of solutions of diazosulphanilic acid in the free state and in the presence of less than one equivalent of alkali. A. H.

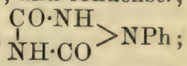
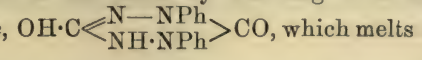
**Intramolecular re-arrangement of Diazonium Thiocyanates.** By ARTHUR R. HANTZSCH and BENNO HIRSCH (*Ber.*, 1896, **29**, 947—952).—Diazonium thiocyanates are prepared from diazonium salts and potassium thiocyanate in alcoholic or aqueous solution; the solubility diminishes as the number of haloïd elements in the benzene nucleus increases; they resemble the diazonium salts in general properties, but differ from the diazo-cyanides. Diazonium thiocyanates, containing one or more haloïd elements in the benzene nucleus, undergo, more or less readily, intramolecular re-arrangement, the haloïd atom changing place with the group SCN; the resulting compounds are less strongly coloured and not nearly so explosive as the original thiocyanates.

*Benzenediazonium thiocyanate*, $N{:}NPh{\cdot}SCN$, is prepared from potassium thiocyanate and benzenediazonium chloride in absolute alcoholic solution below 0°; it is a yellow, highly explosive compound, moderately stable in aqueous solution; it readily combines with alkaline β-naphthol solution, and slowly decomposes into phenol, nitrogen, and hydrogen thiocyanate. *Parachlorobenzenediazonium thiocyanate*, prepared in a similar manner to the preceding compound from neutral parachlorobenzenediazonium chloride (see below), is much less soluble, and does not explode so readily; it may be filtered, and rubbed on a porous plate if moist, but when almost dry it decomposes with great ease.

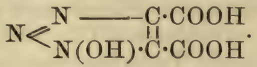
*Parathiocyanobenzenediazonium chloride*, $NCS{\cdot}C_6H_4{\cdot}NCl{:}N$, is formed almost instantaneously by adding a few drops of hydrochloric acid to the preceding compound in alcoholic solution; it crystallises in yellow plates, softens at 104°, explodes at 110—114°, and decomposes slowly at the ordinary temperature. *Parachlorothiocyanobenzene*, $NCS{\cdot}C_6H_4Cl$, is obtained by the action of cuprous chloride on the diazonium chloride; it crystallises in colourless needles, melts at 35—36°, and is readily soluble; its vapour quickly attacks the eyes. This is the first instance of the preparation of a solid thiocyanate of the benzene series. *Tribromobenzenediazonium thiocyanate*, $N{:}N(C_6H_2Br_3){\cdot}SCN$, may, owing to its sparing solubility, be prepared in aqueous solution. Neutral parachlorobenzenediazonium chloride is obtained by the action of amylic nitrite and a little anhydrous hydrogen chloride on parachloraniline hydrochloride in presence of absolute alcohol; the salt, after repeated solution in alcohol and precipitation with ether, softens at 60°, melts and decomposes at 70°, and is very hygroscopic.
J. B. T.

**Diazonium.** By ARTHUR R. HANTZSCH (*Ber.*, 1896, **29**, 1067—1074).—The diazonium group must be taken to correspond with the ammonium group and the alkali metals, since it forms neutral and strongly dissociated salts with the strong acids, and also forms stable salts with weak acids. Its behaviour is in every respect analogous to that of the quaternary ammonium bases. Like the ammonium group, it is extremely unstable in the absence of acid ions. Hydroxyl ions convert it into the syndiazo-group.

Three classes of diazo-compounds are now to be distinguished. The diazonium compounds, which have the constitution $Ph{\cdot}NX{:}N$, the syndiazo-compounds,  $\begin{matrix} Ph{\cdot}N \\ \| \\ R{\cdot}N \end{matrix}$, and the antidiazo-compound,  $\begin{matrix} Ph{\cdot}N \\ \| \\ N{\cdot}R \end{matrix}$.
A. H.

**Unsymmetrical α-Phenylhydrazine Compounds.** By HANS RUPE (*Ber.*, 1896, **29**, 829).—Unsymmetrical *ethylic phenylhydrazidoformate*, $NH_2{\cdot}NPh{\cdot}COOEt$, can be obtained by treating acetylphenylhydrazine with ethylic chloroformate, and hydrolysing the resulting acetyl compound. Its *benzylidene derivative* melts at 96—97°; with cyanic acid, it yields *ethylic phenylsemicarbazidecarboxylate*, $NH_2{\cdot}CO{\cdot}NH{\cdot}NPh{\cdot}COOEt$, which melts at 165—166°, and condenses, under the influence of zinc chloride, to phenylurazole,  $\begin{matrix} CO{\cdot}NH \\ | \\ NH{\cdot}CO \end{matrix}\!\!>NPh$; its *hydrochloride* yields with potassium thiocyanate a *thiocarbamide* melting at 221°; and it condenses with carbonyl chloride to form *ethylic diphenylcarbazidodicarboxylate*, $CO(NH{\cdot}NPh{\cdot}COOEt)_2$, which melts at 159°, and is converted by warming with alkalis into a *tetrazine derivative*,  $OH{\cdot}C{<}\begin{matrix} N{-}NPh \\ NH{\cdot}NPh \end{matrix}{>}CO$, which melts at 263—264°.
C. F. B.

**Orthodinitroso-derivatives of the Benzene Series.** By THEODOR ZINCKE (*J. pr. Chem.*, 1896, [2], **53**, 340—343).—By heating benzeneazimidole (Nietzki, Abstr., 1895, i, 135) with hydriodic acid, it is converted into azimidobenzene; by oxidation with potassium permanganate, it yields a strong tribasic acid,



$$N<\begin{matrix}N\text{———}C\cdot COOH\\ \quad\ \ \ \| \\ N(OH)\cdot C\cdot COOH\end{matrix}.$$

Orthonitrohydrazines are easily converted by nitrous acid into orthonitrodiazoimides, and these lose two atoms of nitrogen when heated, yielding characteristic compounds which appear to be orthodinitroso-derivatives; the following have been prepared: *orthodinitrosobenzene*, $C_6H_4(NO)_2$ (m. p. 71°); *orthodinitrosotoluenes*, [$Me : (NO)_2 = 1 : 3 : 4$ and $1 : 2 : 3$ respectively] (m. p. 96—97° and 60° respectively); *orthodinitroso-xylene*, [$Me_2 : (NO)_2 = 1 : 3 : 4 : 5$] (m. p. 108—109°). Reducing agents convert these dinitroso-compounds into diamines, ortho-dioximes, apparently, being intermediate products. *Benzeneorthodioxime*, $C_6H_4(N\cdot OH)_2$, crystallises in yellowish needles, melts at 142°, and combines with both acids and bases to form intensely red salts; on oxidation, it yields dinitrosobenzene, and on treatment with hot alkalis, it gives an anhydride, $C_6H_4<^{N}_{N}>O$, which yields an acid, probably furazanedicarboxylic acid, on oxidation.

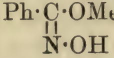
A. G. B.

**Reduction of the Nitro- to the Hydroxylamine Group.** By EUGEN BAMBERGER and MAJA KNECHT (*Ber.*, 1896, **29**, 863—864).—The preparation of hydroxylamine derivatives from nitro-compounds may be carried out by the use of aluminium sulphate and a 5 per cent. zinc amalgam with excellent results. Nitrobenzene thus yields 85 per cent. of the theoretical yield (compare Wislicenus, this vol., i, 298).

A. H.

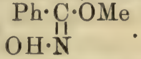
**Stereoisomeric Benzhydroximic acid Derivatives.** By ALFRED WERNER (*Ber.*, 1896, **29**, 1146—1153).—Lossen's criticisms (Abstr., 1895, i, 37) of the author's previous work are answered. Three modifications of methylbenzhydroximic acid are known, one (m. p. 64°) was prepared by Lossen and Zanni, and termed the α-acid. Lossen has since failed to prepare it, but it proves to be the anti-compound (compare following abstract); the second melts at 44°, and is the syn-compound; the third, Lossen's β-acid, melts at 101°. The relationship between the α- and β-acids is very intimate; the α- is converted into the β-compound by the slightest trace of the latter, therefore special care is necessary in working with the α-compound, as the room, the atmosphere, and the clothes of the experimenter, must be perfectly free from the β-acid. Both compounds yield identical derivatives, and the α-acid is regenerated from these if the above precautions are observed. The molecular weight of the β-acid, in ethereal and in glacial acetic acid solution, corresponds with the simple formula.

J. B. T.

**Stereoisomeric Derivatives of Benzhydroximic acid.** By ALFRED WERNER and J. SUBAK (*Ber.*, 1896, **29**, 1153—1161; compare preceding abstract).—Methylantibenzhydroximic acid is prepared from benzimidomethyl ether and hydroxylamine; a mixture of two acids is first obtained, which may either be separated in the manner described below, or converted by means of the benzoyl derivative into the anti-acid (m. p. 64°); by the action of phosphorus pentachloride, it yields an *ethereal phosphate*, $PO(O\cdot N\dot{:}CPh\cdot OMe)_3$, which is crystalline, melts at 83°, and indicates that the compound has the anti-configuration,  $\begin{array}{l}Ph\cdot C\cdot OMe\\ \quad\;\,\|\\ \quad\;\, N\cdot OH\end{array}$. The benzoyl derivative crystallises in small needles, melting at 54°, and has been previously prepared by Lossen (Abstr., 1895, i, 37). The *benzenesulphonate*,

$$OMe\cdot CPh\dot{:}N\cdot O\cdot SO_2Ph,$$

crystallises in needles, melting at 72°. The *dinitrophenyl* derivative, $OMe\cdot CPh\dot{:}NO\cdot C_6H_3(NO_2)_2$ [$O : NO_2 : NO_2 = 1 : 2 : 4$], crystallises in slender, pale yellow needles, melting at 121°. The *paramethoxybenzoyl*- and *carbanilido*-derivatives are crystalline, and melt at 55° and 115° respectively.

The methylbenzhydroximic acid prepared by Lossen from methylic iodide and silver benzoylbenzhydroximate (dibenzhydroximate), which melts at 63°, is a mixture of both stereoisomerides; these are separated by dissolving the acid in potash, and extracting the solution about 30 times with ether; the anti-acid dissolves first, then a mixture of both, and finally the *syn-acid;* this crystallises in small needles, melts at 44°, and slowly liquefies at the ordinary temperature, a portion changing into the anti-compound. By the action of phosphorus pentachloride, a chloro-derivative is obtained, which undergoes Beckmann's reaction, and, with sulphuric acid, is resolved into aniline, methylic benzoate, phenylmethylurethane, hydrogen chloride, and carbonic anhydride, thus proving the configuration of the original acid to be  $\begin{array}{l}\quad\;\, Ph\cdot C\cdot OMe\\ \qquad\quad\|\\ \quad OH\cdot N\end{array}$. The *benzoyl* derivative, prepared in presence of potash in large excess, is crystalline, and melts at 55°. The 1 : 2 : 4-*dinitrophenyl* derivative is more readily soluble in light petroleum than the anti-compound; it crystallises in yellow needles, melting at 122—125°; a mixture of both isomerides melts about 20° lower. The *paramethoxybenzoyl* derivative crystallises in colourless plates, melting at 96—98°. The *carbanilido*-derivative is crystalline, and melts at 117°; when mixed with the anti-compound, the melting point falls about 20°. J. B. T.

**Ethylenedihydroxylamine.** By ALFRED WERNER and A. GEMESEUS (*Ber.*, **29**, 1896, 1161—1164).—Benzenylamidoxime ethylenic ether, $C_2H_4(O\cdot N\dot{:}CPh\cdot NH_2)_2$, prepared from benzenylamidoxime, sodium ethoxide, and ethylenic bromide, crystallises from dilute alcohol in lustrous plates, which melt at 161°, and not at 155—156°, as previously stated. The *dichloro*-derivative,

$$C_2H_4(O\cdot N\dot{:}CPhCl)_2,$$

is formed by the action of hydrochloric acid and sodium nitrite on the preceding compound; it crystallises in prisms, and melts at 59—60°. The *dibromo*-derivative, prepared in a similar manner by means of hydrobromic acid, crystallises from a mixture of alcohol and ether in long, thin, silky, lustrous needles, melting at 100°; by prolonged contact with water it is converted into an isomeric modification, which is also formed in small quantity with the original substance; the isomeride is readily soluble in ether, crystallises from glacial acetic acid in needles, and melts at 81—82°. *Ethylenic ethylbenzhydroximate*, $C_2H_4(O·N\colon CPh·OEt)_2$, is obtained by the action of sodium ethoxide on either of the above haloïd compounds; it is a brownish oil, with an aromatic odour, and was not completely purified; when hydrolysed by means of concentrated hydrochloric acid, it yields benzoic acid, and *ethylenedihydroxylamine hydrochloride*, $C_2H_4(O·NH_2)_2,2HCl$, which crystallises in plates. J. B. T.

**Preparation of Valeranilide using Phosphorus Trichloride.** By ENRICO SPIZZICHINO and CARLO CONTI (*L'Orosi*, 1895, **18**, 262—263).—*Valeranilide*, $C_3H_7·CH_2·CO·NHPh$, is readily obtained with development of heat by slowly adding phosphorus trichloride to a mixture of aniline and valeric acid; it crystallises from alcohol in beautiful white, odourless needles, melting at 103—105°. It is soluble in alcohol, ether, or chloroform, but insoluble in water, and is hydrolysed on fusion with potash. W. J. P.

**Products of the Chlorination of Benzaldehyde and their Derivatives.** By ROBERT GNEHM and E. BÄNZIGER (*Ber.*, 1896, **29**, 875—878).—When benzaldehyde is treated with iodine and antimony pentachloride (American patent, No. 315,932), the product contains ortho- and meta-chlorobenzaldehyde, 3 : 4- and 2 : 5-dichlorobenzaldehyde, and perchlorobenzene. A certain amount of tetrachlorobenzene is formed during the fractionation of the chloraldehydes. The following derivatives of 2 : 5-dichlorobenzaldehyde were prepared. The *phenylhydrazone* melts at 104—105°; the *aniline compound* crystallises in white, nacreous plates, melting at 71·5—72°; the *paraphenetidine compound* melts at 59°; the *methylamine compound* crystallises in nacreous plates, and melts at 52°. The aldehyde forms a condensation product with dimethylaniline, which is the *leuco-base* of the colouring matter contained in "new solid green 3B"; it crystallises from benzene in vitreous plates, and melts at 179°.

2 : 5-Dichlorobenzaldehyde is converted by nitration into orthonitrodichlorobenzaldehyde $[CHO : Cl_2\colon NO_2 = 1 : 2 : 5 : 6]$ (*Ber.*, **17**, 752), and an isomeric substance melting at 66·5°. The latter yields an *oxime*, which crystallises in long, white needles, melting at 93°, and a *phenylhydrazone*, which forms slender, orange-coloured needles, and melts at 174°. The *aniline compound* crystallises in faintly yellow, thin tablets, and melts at 113—114°.

The *oxime* of orthonitrodichlorobenzaldehyde crystallises in long, white needles, and melts at 154—155°; the *phenylhydrazone* forms slender needles, melting at 146—147°, and the *aniline compound* melts at 102—103°. Orthonitrodichlorobenzaldehyde can readily be reduced to the corresponding amido-derivative, which yields an *oxime*, melting at 175—176°, and a *phenylhydrazone*, melting at 102—103°. This base could not be converted into a hydroxy-compound by means of the diazo-reaction.

When the orthonitro-compound is treated with sodium sulphite, the nitro-group is eliminated, and a substance is formed which does not contain nitrogen.

The mixture of chloraldehydes which is referred to above is used for the manufacture of colouring matters. "New solid green 3B" is a mixture of the nitrate and hydrochloride of the colour base derived from tetramethyldiamidodichlorotriphenylcarbinol,

$$C_6H_2Cl_2\cdot C(OH)(C_6H_4NMe_2)_2.$$

"New solid green 2B" consists of a mixture of the hydrochloride just mentioned, and the corresponding monochloro-derivative. "Firn blau" is the hydrochloride of the colour base of dimethyldiamidodiorthotolyldichlorophenylcarbinol.

A. H.

**Preparation of Mono- and Di-acetyl Derivatives of Aromatic Hydrocarbons.** By VICTOR MEYER (*Ber.*, 1896, **29**, 846—848).—The use of the method previously given by Meyer and Baum (this vol., i, 228) for the preparation of monacetyl derivatives sometimes resulted in the formation of diacetyl derivatives. In order to avoid this, it is advisable to vary the amount of aluminium chloride employed in the two cases, instead of the time of heating as was previously done.

The constitution of diacetylisodurene has been confirmed by the author in conjunction with Seymour, so that this substance is a 1 : 5-diketone.

A. H.

**New Experiments on the Law of Formation of Oximes, Hydrazones, and Ethereal Salts.** By VICTOR MEYER (*Ber.*, 1896, **29**, 830—839).—Many of Claus' statements (Abstr., 1888, 275; and this vol., i, 230) are entirely erroneous. Acetylisodurene [$Me_4 : Ac = 1:3:4:5:6$] yields neither a hydrazone nor an oxime. Acetyldurene [$1:2:4:5:6$] melts at 73° (Claus 63°) and does not form a hydrazone. Durenecarboxylic acid [$Me_4 : COOH = 1:2:4:5:6$] was prepared long ago by Jacobsen (Abstr., 1889, 877), and does not melt at 127°, but at 178°; it is not readily etherified, but it yields 60 per cent. of the methylic salt when treated with gaseous hydrogen chloride in boiling methyl alcoholic solution. Isodurenecarboxylic acid [$1:3:4:5:6$] is not an oil, but forms good crystals, and melts, even in the crude state, above 150°.

The influence of the grouping $C_6H_3Me_2\cdot CO\cdot R$, [$CO : Me_2 = 1:2:6$] on the power to form an oxime or hydrazone has been studied, in the case of mesitylene derivatives, $C_6H_2Me_3\cdot CO\cdot R$. When $R = H$, or COOH, oximes and hydrazones are formed; these are not formed when $R =$ Me, Et, $Pr^{\alpha}$, $P^{\beta}$, Ph, $CH_2Cl$, $CHCl_2$, $CCl_3$, $CH_2\cdot CH_2\cdot COOH$.

Alkylic mesitylglyoxylates do really yield oximes (compare Baum, this vol., i, 222); this was shown by preparing the oxime of the amylic salt, the analysis of which leaves no doubt as to its composition.

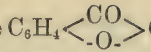
Mesitylenecarboxylic acid (compare this vol., i, 228), when gaseous hydrogen chloride is passed through its alcoholic solution at 0°, yields in seven days and nights, 26 per cent., in double the time 46 per cent., of ethereal salt. Symmetrical trinitrobenzoic acid yields no methylic salt, even when treated for 30 days in this way. It appears that the groups OH and Me in the ortho-positions retard the formation of an ethereal salt, whilst Cl, Br, I, $NO_2$ prevent it altogether. C. F. B.

**Fluorine and the Law of Etherification.** By J. VAN LOON and VICTOR MEYER (*Ber.*, 1896, **29**, 839—845).—It was thought probable, from stereochemical considerations, that the influence of fluorine might not resemble that of the chemically similar radicles Cl, Br, I, and $NO_2$ (compare preceding abstract), but rather approximate to that of Me and OH, which, like it, have a low atomic weight, although their chemical character is different. This was confirmed by experiment; the acid, $NO_2{\cdot}C_6H_3F{\cdot}COOH$ [$COOH : F : NO_2 = 1 : 2 : 6$] yields no ethereal salt when treated with alcoholic hydrogen chloride in the cold; but it yields 67 per cent. when gaseous hydrogen chloride is passed through its boiling alcoholic solution, under which circumstances the corresponding acid containing Cl in place of F yields no ethereal salt. The radicle F thus resembles Me and OH in that, when present in the ortho-position relatively to the COOH group, it only retards the formation of an ethereal salt, and does not, like Cl, Br, I, and $NO_2$, altogether prevent it.

It is pointed out that in stereochemical considerations, we are not concerned with molecular volumes in the sense understood by Kopp. With certain reservations, the atomic weight of a radicle conditions its stereochemical action. But the radicle cetyl, $CH_2{\cdot}[CH_2]_{14}{\cdot}CH_3$, does not resemble the heavy radicles I, &c., in its influence on etherification, but has the same influence as the light radicle $CH_3$, only that $CH_2$ group nearest to the benzene ring coming into play. The radicle $NO_2$, however, acts with its whole weight, and not by virtue of the N atom alone, which would necessitate its being classed with the light radicles. C. F. B.

**A New Method of Formation of Trimethylmandelic [symmetrical Trimethylphenylacetic] acid.** By VICTOR MEYER and CARL SOHN (*Ber.*, 1896, **29**, 846).—When acetomesitylene is reduced with faintly alkaline potassium permanganate solution, symmetrical trimethylphenylacetic acid is sometimes formed, under conditions which have not been definitely ascertained, instead of mesitylglyoxylic acid, which is the usual product of the action. A. H.

**Dry Distillation of Calcium Phenylsalicylate [Orthophenoxybenzoate].** By BERTHOLD JEITELES (*Monatsh.*, 1896, **17**, 65—67).—Calcium orthophenoxybenzoate is distilled in an atmosphere of hydrogen; the product is treated with soda, which dissolves some quantity of phenol, and extracted with ether. On evaporation, the ethereal extract yields a substance crystallising from dilute alcohol in long needles melting at 172—173°, and a yellow oil boiling at 248—251°.



The former substance proves to be xanthone $C_6H_4{<}\substack{CO\\ \text{-}O\text{-}}{>}C_6H_4$, and the latter is identical with phenylic ether $(C_6H_5)_2O$. A. L.

**Benzoylsalicylic acid.** By HEINRICH LIMPRICHT (*Annalen*, **290**, 164—171).—*Parabenzoylsalicylic acid*, $COPh{\cdot}C_6H_3(OH){\cdot}COOH$, is obtained in the form of an alkylic salt when benzoic chloride acts on ethereal salts of salicylic acid in carbon bisulphide solution under the influence of aluminium chloride; it crystallises from alcohol in slender needles, and melts at 210°. Ferric chloride develops a violet coloration in the aqueous solution, and when the dry substance is distilled from lime, parahydroxybenzophenone is produced. The *barium hydrogen* salt crystallises in leaflets, and the *barium* salt in green needles. The *methylic* and *ethylic* salts melt at 92° and 97° respectively, and the latter gives rise to the *potassium* derivative which crystallises in greenish-yellow leaflets; ethylic iodide converts the potassium compound into the *ethyl* derivative,

$$COPh{\cdot}C_6H_3(OEt){\cdot}COOEt,$$

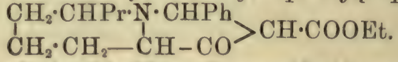
which crystallises from petroleum in aggregates of needles, and melts at 56°. The *ethyl* derivative of benzoylsalicylic acid, *parabenzoylorthoethoxybenzoic acid*, $COPh{\cdot}C_6H_3(OEt){\cdot}COOH$, is obtained from the foregoing compound by hydrolysis; it crystallises from dilute spirit in small needles, and melts at 109°.

*Phenylic benzoylsalicylate* (*benzoylsalol*), $COPh{\cdot}C_6H_3(OH){\cdot}COOPh$, is obtained by heating benzoylsalicylic acid and phenol with phosphorus oxychloride; it crystallises in lustrous, monoclinic plates, and melts at 84°. The *benzoic* derivative of ethylic salicylate, $OBz{\cdot}C_6H_4{\cdot}COOEt$, is produced on heating ethylic orthoethoxybenzoate with benzoic chloride, carbon bisulphide, and aluminium chloride; it crystallises in large, colourless plates melting at 79°, and is identical with Freer's ethylic benzoylsalicylate (Abstr., 1893, i, 66). The *benzoic* derivative of ethylic benzoylsalicylate, $COPh{\cdot}C_6H_3(OBz){\cdot}COOEt$, is obtained from benzoic chloride and the sodium derivative of ethylic benzoylsalicylate; it crystallises in leaflets, and melts at 87°.

*Metanitroparabenzoylsalicylic acid* is obtained in the form of its ethylic salt when ethylic salicylate, carbon bisulphide, and metanitrobenzoic chloride are heated with aluminium chloride; it crystallises in small, lustrous prisms, and melts at 244°. The *ethylic* salt, to which reference has been made, crystallises in transparent leaflets, and melts at 116°.

Ethylic metahydroxybenzoate and its potassium and ethyl derivatives, when treated with benzoic chloride and aluminium chloride, yield the *compound*, $OBz{\cdot}C_6H_4{\cdot}COOEt$, which crystallises from alcohol in long, white needles, and melts at 58°; boiling caustic soda gives rise to benzoic and metahydroxybenzoic acids. M. O. F.

**Reaction of Aromatic Bases with Ethylic Benzylidenemalonate and Furfurylidenemalonate.** By I. GOLDSTEIN (*Ber.*, 1896, **29**, 813—818; compare Abstr., 1895, i, 470).—Ethylic benzylidenemalonate forms, with unsymmetrical methylphenylhydrazine, a crystalline additive compound, *ethylic β-phenylmethylhydrazidobenzylmalonate*, $NMePh\cdot NH\cdot CHPh\cdot CH(COOEt)_2$. This yields a *hydrochloride*, which is decomposed by water; hydrolysis converts it into the *dipotassium salt*, but when an attempt is made to liberate the acid from this salt, benzylidenemethylhydrazine, $NMePh\cdot N{:}CHPh$, and malonic acid are obtained instead. A similar additive compound, *ethylic β-piperidobenzylmalonate*, $C_5NH_{10}\cdot CHPh\cdot CH(COOEt)_2$, melting at 58—59°, is formed with piperidine; the *hydrochloride* and *dipotassium salt* were prepared, but the free acid does not exist; it breaks up into piperidine, benzaldehyde, and malonic acid. This additive-compound yields a *tri*-sodium salt when treated with alcoholic sodium ethoxide, which shows that, in the process of addition, the hydrogen atom must have gone to the α-carbon atom. With coniine, ethylic benzylidenemalonate yields *ethylic phenylpropyltetrahydroazindonecarboxylate*,



$$\begin{array}{l} CH_2\cdot CHPr\cdot N\cdot CHPh \\ \big| \qquad\qquad\quad \big| \\ CH_2\cdot CH_2-CH-CO \end{array}\!\!>CH\cdot COOEt.$$

This melts at 150—152°; its *platinochloride* and *aurochloride* were prepared. The free *acid* melts at 85°, and at 95° loses carbonic anhydride, forming *phenylpropyltetrahydroazindone*, which melts at 212°; the *lead salt* of the acid crystallises with $H_2O$.

Piperidine also forms, with ethylic furfurylidenemalonate, an additive compound, $C_4OH_4\cdot CH(C_5NH_{10})\cdot CH(COOEt)_2$, which melts at 35—37°.
C. F. B.

**Ethylic α- and β-Benzoyltricarballylates.** By WILLIAM O. EMERY (*J. pr. Chem.*, 1896, [2], **53**, 312—314).—*Ethylic α-benzoyltricarballylate*, $COOEt\cdot CHBz\cdot CH(COOEt)\cdot CH_2\cdot COOEt$, is prepared by heating a mixture of sodium (2·4 grams) dissolved in absolute alcohol (30 grams), ethylic benzoylacetate (20 grams), and ethylic chlorosuccinate (22 grams), on the water bath for half an hour. It is a greenish, fluorescent oil which distils at 250° (at 16 mm.), and has a sp. gr. = 1·14557 at 20°/4°; strong hydrochloric acid converts it into phenacylsuccinic acid (m. p. 156—157°) which yields an anhydride, $C_{12}H_{10}O_4$, melting at 147—148°, and is obtainable by other methods to be elucidated presently.

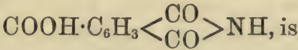
*Ethylic β-benzoyltricarballylate*, $COOEt\cdot CBz(CH_2\cdot COOEt)_2$, is similarly prepared from sodium ethoxide, ethylic benzoylsuccinate, and ethylic bromacetate. It is a light, yellow oil which boils at 225° (at 14 mm.); its sp. gr. = 1·14783 at 20°/4°. Prolonged heating with strong hydrochloric acid converts it into β-benzoylglutaric acid.
A. G. B.

**Dicarboxyphenylglyoxylic acid.** By CARL GRAEBE and FR. BOSSEL (*Annalen*, 1896, **290**, 206—216; compare Abstr., 1893, i, 593).—The *barium* and *calcium* salts of dicarboxyphenylglyoxylic acid contain $4H_2O$, the *potassium* salt crystallises from water in leaflets, and the *silver* salt is sparingly soluble in water; the *dimethylic* and *trimethylic* salts melt at 154—156° and 168°, respectively. The phenylhydrazone (*loc. cit.*) crystallises in colourless leaflets, and melts at 205—208°.
M. O. F.

**Hemimellitic acid.** By Carl Graebe and Max Leonhardt (*Annalen*, 1896, **290**, 217—238).—Graebe and Bossel have shown that hemimellitic acid is produced on oxidising dicarboxyphenylglyoxylic acid (Abstr., 1893, i, 593; also foregoing abstract), which, therefore, is a convenient source of the acid in question.

Hemimellitic acid crystallises from water in plates, containing $2H_2O$; it melts at 190°, being converted into the *anhydride* $C_9H_4O_5$, which melts at 196°, and yields carbonic and phthalic anhydrides above 300°. The *monopotassium* salt is precipitated in leaflets on adding aqueous potassium chloride to a cold, saturated solution of the acid; it contains $2H_2O$, and dissolves in 170 parts of water at 17°. The *tripotassium* salt crystallises in needles, and dissolves very readily in water; the barium salt contains $6H_2O$.

Although, in accordance with Victor Meyer's generalisation, direct etherification of hemimellitic acid gives rise to the dimethylic salt alone, methylic alcohol converts the anhydride into a monomethylic salt, whilst further action of the alcohol, under the influence of hydrogen chloride, leads to the trimethylic salt. The *monomethylic* salt crystallises from water in needles, and melts at 203—205°, the *dimethylic* salt melts at 145°, and does not decompose when distilled, and the *trimethylic* salt melts at 100°.

The *imide* of hemimellitic acid,  $COOH{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}NH$, is obtained by the action of ammonia on the anhydride, and crystallises from water in colourless needles melting at 247° (corr.). The *silver* salt is colourless, and the *calcium* salt crystallises in leaflets, and contains $1\frac{1}{2}H_2O$.

*Benzoylphthalic acid* $[COOH_2 : COPh = 1 : 2 : 3]$ is obtained by heating the anhydride of hemimellitic acid with aluminium chloride and benzene in a reflux apparatus; it crystallises from water in colourless needles containing $1H_2O$, and effervesces at 130—140°, yielding the *anhydride* which melts at 183° (corr.). The solution in cold concentrated sulphuric acid is bright yellow, becoming olive-green at 145—150°, 1-anthraquinonecarboxylic acid being formed; this substance melts at 293—294° (corr.), and the *ethylic* salt crystallises from alcohol in yellow needles melting at 169°. *Benzoylisophthalic acid* $[COOH : COPh : COOH = 1 : 2 : 3]$ is prepared by heating monopotassium hemimellitate with aluminium chloride and benzene, and crystallises from dilute alcohol in needles melting at 260°; concentrated sulphuric acid converts it into 1-anthraquinonecarboxylic acid. *Dibenzoylbenzoic acid* $[COOH : COPh_2 = 1 : 2 : 3]$ is produced along with benzoylphthalic acid, and melts at 208°; phthalophenone is formed on submitting the substance to dry distillation. *Dibenzoylbenzoic acid* $[COOH : COPh_2 = 1 : 2 : 6]$ is obtained when the action of benzene and aluminium chloride extends over a shorter period; it melts at 100°.

When hemimellitic anhydride is heated with resorcinol for two hours at 200°, two fluoresceïncarboxylic acids are produced, one of which yields an anhydride; on extracting the powdered mass with boiling water, and, on cooling, the 6-*fluoresceïncarboxylic acid*, $C_{21}H_{12}O_7$, is deposited in yellow needles; it does not melt at 280°, and the solutions in alkalis exhibit very feeble fluorescence. The *anhydride* of 3-fluoresceïncarboxylic acid, $C_{21}H_{10}O_6$, is obtained by dissolving the residue in sodium carbonate and precipitating with hydrochloric acid; the solutions in alkalis are yellowish-red, and exhibit feeble fluorescence. The *acetyl* derivative is crystalline, and melts above 300°.

When hemimellitic anhydride is heated with metadimethylamidophenol, a *rhodamine* is produced which dissolves in alkalis forming a violet-red solution. M. O. F.

**Derivatives of Sulphometabromobenzoic acid.** By CARL BOETTINGER (*Arch. Pharm.*, 1896, **234**, 47—55).—*Chlorosulphometabromobenzoic chloride*, $SO_2Cl{\cdot}C_6H_3Br{\cdot}COCl$ [5 : 3 : 1], is prepared by heating potassium or calcium sulphometabromobenzoic acid with phosphorus pentachloride, dissolving in ether, and washing out the phosphorus oxychloride with water; it crystallises in long, colourless needles, and melts at 64°. The *amido*-derivative,

$$NH_2{\cdot}SO_2{\cdot}C_6H_3Br{\cdot}CONH_2,$$

forms hard, glistening crystals, with $1H_2O$, and, when anhydrous, melts at 198·5—199·5°. By heating it with dilute caustic soda solution, it is converted into *sodium sulphamidometabromobenzoate;* the free acid crystallises in long, colourless needles, and melts at 251°. On acidification, the mother liquor from the crystallisation of the diamide yields a second *amido*-acid which crystallises in thick prisms, and melts at 237—238°.

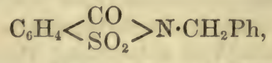
*Chlorosulphometabromobenzoic acid* can be isolated from the mass obtained in preparing the foregoing chloride; it forms thick, white crystals, melts at 170°, and is nearly insoluble in light petroleum, sparingly soluble in cold alcohol, and more freely in ether.

*Sulphimetabromobenzoic acid*, $SO_2H{\cdot}C_6H_3Br{\cdot}COOH$, is obtained by reducing chlorosulphometabromobenzoic acid with zinc dust in alcoholic solution. It crystallises from hot water in slender needles, and melts at 202°.

A postscript contains some remarks on Heyl and V. Meyer's recent paper on the benzene problem (this vol., i, 145).

A. G. B.

**Derivatives of Orthobenzoicsulphinide (Saccharin).** By HUGO ECKENROTH and GEORG KOERPPEN (*Ber.*, 1896, **29**, 1048—1051; compare this vol., i, 304).—*Benzylorthobenzoicsulphinide*,



$$C_6H_4{<}\begin{matrix}CO\\SO_2\end{matrix}{>}N{\cdot}CH_2Ph,$$

crystallises in colourless needles melting at 118°, and has not a sweet taste. *Benzylorthamidosulphobenzoic acid*, $COOH{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}CH_2Ph$, is an uncrystallisable oil; the *sodium salt* crystallises in rosettes of small needles, and the *barium salt* is a crystalline powder. *Paranitrobenzylorthobenzoicsulphinide* forms slender, light yellow needles, and melts at 175·5—176°. *Paranitrobenzylorthamidosulphobenzoic acid* forms yellowish crystals, and melts at about 170°; the *potassium salt* crystallises in colourless rhomboids. *Acetylorthobenzoicsulphinide* is formed by the action of acetic anhydride on sodium benzoicsulphinide, whilst benzoicsulphinide itself is always formed by the action of acetic chloride. It crystallises in white, lustrous plates, and, when warmed with aqueous soda, yields sodium acetate and benzoicsulphinide, and not a sulphobenzoic acid. When sodium benzoicsulphinide is heated with ethylenic bromide and a little alcohol, it yields ethylenediorthobenzoicsulphinide in small quantity, along with *bromethylorthobenzoicsulphinide*, $C_6H_4<\substack{SO_2\\CO}>N\cdot C_2H_4Br$. The latter crystallises in white needles melting at 96°. A. H.

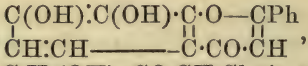
**Dissociation of Diazosulphonates [Correction].** By EUGEN BAMBERGER (*Ber.*, 1896, **29**, 1052).—The author points out that he was in error in his criticism (this vol., i, 373) of the calculation of certain of the results obtained by Hantzsch by means of the cryoscopic method (Abstr., 1895, i, 664). A. H.

**The Ionic Dissociation of the Diazosulphonates.** By ARTHUR R. HANTZSCH and DIMITER GERILOWSKI (*Ber.*, 1896, **29**, 1057—1058; compare the foregoing abstract).—The criticism of Bamberger (this vol., i, 373) is founded on a miscalculation, the numbers obtained by the authors being perfectly correct. A. H.

**Stereoisomeric Salts of Orthodiazobenzenesulphonic acid.** By DIMITER GERILOWSKI (*Ber.*, 1896, **29**, 1075—1078).—*Diazoniumbenzeneorthosulphonic acid*, $N\colon N<\substack{O\,-\\C_6H_4}>SO_2$, is a yellowish, crystalline substance, which is more readily soluble in water than the para-compound, and detonates gently when it is heated. *Sodium syndiazobenzeneorthosulphonate* is prepared in a manner similar to the corresponding para-salt (Abstr., 1895, i, 664). It forms white, silky needles, and may be preserved in dry air, but becomes red, and then deliquesces in the atmosphere. It readily yields a colouring matter with $\beta$-naphthol, which produces a yellow shade of red. The *anti-salt* is more soluble in water than the syn-salt, and has not been obtained in the solid state.

*Potassium syndiazobenzeneorthosulphonate*, $SO_3K\cdot C_6H_4\cdot N_2\cdot OK + \frac{1}{2}H_2O$, is a yellowish powder. The *anti-salt*, obtained by boiling the syn-salt with the mother liquor from its preparation, crystallises in groups of radiating needles. As in the para-series, the two salts behave differently towards hydrochloric acid; the syn-salt is immediately converted into the diazonium-compound, whilst this change only occurs slowly with the anti-salt, the solution of which is, therefore, rendered acid by the addition of hydrochloric acid, and only slowly becomes neutral. A. H.

**Preparation of Flavone Derivatives.** By PAUL FRIEDLÄNDER and HERMANN RÜDT (*Ber.*, 1896, **29**, 878—880).—Benzaldehyde reacts with orthohydroxyacetophenone alcohols, or their chlorides to form condensation products which are closely related to the flavone derivatives, such as chrysin and the colouring matters of quercitron bark and fustic ("fustet.")

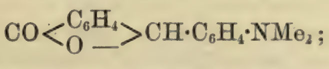
*Dihydroxyflavone*,  $\begin{array}{l} C(OH){:}C(OH){\cdot}C{\cdot}O{-}CPh \\ CH{:}CH{-\!-\!-\!-}C{\cdot}CO{\cdot}CH \end{array}$, is formed when gallochloracetophenone, $C_6H_2(OH)_3{\cdot}CO{\cdot}CH_2Cl$, is treated with benzaldehyde and aqueous potash. It forms lustrous, yellow plates, and dyes mordanted cloth; the colour being yellow with alumina, and brown with chromium mordants. The *acetyl* compound forms colourless crystals melting at 198—199°. Dihydroxyflavone is isomeric with chrysin, which is a derivative of phloroglucinol. This reaction occurs with a large number of hydroxyacetophenone derivatives, and is being further investigated. A. H.

**New Method of preparing Orthohydroxybenzophenone.** By Carl Graebe and F. Ullmann (*Ber.*, 1896, **29**, 824—825).—This compound is at once obtained by acting on methylsalicylic chloride, $OMe{\cdot}C_6H_4{\cdot}COCl$, with benzene in the presence of aluminium chloride; prepared in this way, it melts at 39—40°. It yields xanthone when heated with lead oxide. Another substance, possibly a dihydroxybenzophenone, is formed at the same time as the monhydroxy-compound; it melts at 127°, and is only sparingly soluble in light petroleum. C. F. B.

**Orthobenzoylphenol [Orthohydroxybenzophenone].** By Paul Cohn (*Monatsh.*, 1896, **17**, 102—109).—Phenylindoxazine is heated with fuming hydriodic acid (sp. gr. = 1·7) and phosphorus in sealed tubes at 140—160° during 6—7 hours; the product is diluted with water, extracted with ether, the ethereal extract being then evaporated, and the residue heated on the water bath with sodium ethoxide. After desiccation, the powdered mass is extracted in a Soxhlet's apparatus with anhydrous ether, when the *sodium* derivative of orthobenzoylphenol, $ONa{\cdot}C_6H_4{\cdot}CO{\cdot}C_6N_5$, is dissolved, and crystallises in small, yellow needles; it dissolves readily in dilute alkali and alcohol, but only sparingly in ether. *Orthobenzoylphenol* [orthohydroxybenzophenone], $OH{\cdot}C_6H_4{\cdot}COPh$, crystallises in leaflets, dissolves sparingly in water, but readily in alcohol, ether, and acetic acid; it melts at 36°, and distils, unaltered, under 560 mm. pressure; it has a characteristic odour, and forms sparingly soluble, yellow barium and calcium compounds; it is violently attacked by warm, dilute nitric acid, and yields explosive nitro-compounds when dissolved in a mixture of nitric and sulphuric acids. It yields salicylic acid when fused with potash.

Orthobenzoylphenol gives a number of characteristic derivatives. Its *dibromo*-derivative, $OH{\cdot}C_6H_2Br_2{\cdot}COPh$, crystallises in beautiful, light-green needles, dissolves sparingly in cold alcohol, readily in hot alcohol and chloroform, and melts at 126°. *Orthomethoxybenzophenone*, $OMe{\cdot}C_6H_4{\cdot}COPh$, formed by the action of methylic iodide at 100° on the potassium derivative, is a yellowish oil sparingly soluble in water and alkalis, readily soluble in alcohol, ether, &c. The *benzoate*, $COPh{\cdot}C_6H_4{\cdot}OBz$, is readily obtained by the Baumann-Schotten method; it forms a yellowish oil which dissolves readily in all solvents, with the exception of water or alkalis. The *phenylhydrazone*, $OH{\cdot}C_6H_4{\cdot}CPh{:}N{\cdot}NHPh$, is formed by the action of phenylhydrazine on the phenol at 150°; it is insoluble in water, acids, or alkalis, sparingly soluble in cold alcohol or ether, but readily in benzene and hot alcohol; from the latter, it crystallises in beautiful, transparent prisms, which have a tendency to aggregate in star-like forms; it melts at 155°. The *oxime*, $OH·C_6H_4·CPh\dot{:}NOH$, dissolves in alkalis, and crystallises from ether; it melts to a colourless liquid at 133—134°. A. L.

**Condensation of Orthophthalaldehydic acid with Dimethylaniline.** By ROBERT EBERT (*Chem. Zeit.*, 1895, **19**, 2039—2040).—Orthophthalaldehydic acid (Racine, Abstr., 1886, 549) is readily soluble in dimethylaniline, and on treating the hot solution with a dehydrating agent, such as zinc chloride, hydrogen chloride, anhydrous oxalic acid, &c., a blue or green colour is developed. The product, after being dissolved in water or dilute acid, and treated with caustic soda, yields a resin, whilst Fischer's dimethylanilinephthalin remains in solution. The resin contains *dimethylamidophenylphthalide*,



$$CO{<}{}^{C_6H_4}_{O\;—}{>}CH·C_6H_4·NMe_2;$$

this melts at 186°, is soluble in ether, benzene, and alcohol, and only sparingly soluble in 50 per cent. alcohol, from which it crystallises in colourless plates. It is readily soluble in hydrochloric acid, and is completely precipitated by alkalis. The solution of the base in sulphuric acid is colourless, but turns first yellow and then orange on warming.

The red or blue colouring matter obtained by the condensation of the aldehydic acid with dimethylaniline in the presence of zinc chloride is probably Fischer's phthalic green. J. J. S.

**Coloured Rosaniline Bases.** By GEORG VON GEORGIEVICS (*Monatsh.*, 1896, **17**, 4—12; compare Abstr., 1895, ii, 257).—The colourless base of pararosaniline, $C_{19}H_{19}N_3O$, may be obtained by adding to a faintly acid solution of magenta (1 gram) in water at 70° (3 litres) a slight excess of alkali, rapidly filtering from the amorphous precipitate, and cooling the filtrate. It is obtained as beautiful shining leaflets, and when moist is stable only in presence of alkali, becoming coloured immediately on its removal. The red modification of the base is obtained on precipitating a cold solution of magenta by a little more than the calculated quantity of alkali, and contains neither chlorine nor carbonic anhydride. The red coloration is not due to the formation of a carbonate, as it becomes apparent even in the complete absence of carbonic anhydride, nor is it attended by any appreciable alteration in composition.

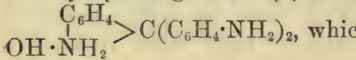
Although the colour of a solution of the coloured base is less intense than that of a corresponding solution of the hydrochloride, yet the dyeing powers of the two appear to be identical, equal weights of silk dyed to the same depth of colour in either solution extracting the same weight of base.

The coloured base, when repeatedly extracted with hot water, becomes darker in colour and less soluble in water. The final product, which bears a marked resemblance to the original substance, gives on analysis numbers agreeing with the formula $C_{19}H_{17}N_3O$, and contains, therefore, two atoms of hydrogen less than the rosaniline base.

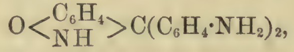
As a result of his experiments, the author concludes that there are three rosaniline bases: (1) a colourless carbinol base,

$$OH\cdot C(C_6H_4\cdot NH_2)_3,$$

readily passing into (2) a magenta coloured ammonium base,



$\begin{matrix}C_6H_4\\ |\\ OH\cdot NH_2\end{matrix}>C(C_6H_4\cdot NH_2)_2$, which is present in the aqueous solution of rosaniline salts, and (3) an imidoxide base,



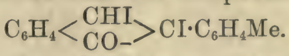
$$O<\begin{matrix}C_6H_4\\ NH\end{matrix}>C(C_6H_4\cdot NH_2)_2,$$

which is more stable and less soluble in water than the ammonium base, and may be obtained from it by the action of hot water.

A. L.

**Action of Bromine, Chlorine and Sulphur on Fluorene.** By CARL GRAEBE and B. VON MANTZ (*Annalen*, 1896, **290**, 238—246; compare Abstr., 1893, i, 38).—When bromine or chlorine acts on fluorene at 115—150°, the halogen enters a phenylene residue, whilst above this temperature methylenic hydrogen is eliminated, and bidiphenylenethylene is produced (*loc. cit.*). The dibromide of the hydrocarbon crystallises from boiling benzene or toluene in colourless plates, and melts and decomposes at 235°; the *dichloride*, $C_{26}H_{16}Cl_2$, also forms colourless crystals, and melts at 234°. Oxidation of bidiphenylenethylene with potassium dichromate and dilute sulphuric acid converts it into fluorenone along with a *compound*, $C_{39}H_{26}O_2$, which separates from glacial acetic acid in pale yellow crystals, and melts at 250—252°; when distilled from zinc dust, bidiphenylene-ethylene yields fluorene.

On heating fluorene with sulphur, hydrogen sulphide is evolved, and bidiphenylethane or bidiphenylethylene is produced according to the amount of sulphur employed. M. O. F.

**Action of Iodoform on β-Naphthol in Sunlight.** By M. C. SCHUYTEN (*Chem. Zeit.*, 1895, **19**, 2164).—When a concentrated ethereal solution of iodoform (1 mol.) is mixed in the dark with α-naphthol (5 mols.), and the resulting mixture exposed in a closely stoppered bottle to bright sunlight, a considerable quantity of a bronze coloured, crystalline substance is deposited, together with a small amount of iodoform. The latter, however, goes into solution again if the mixture is left exposed to sunlight for several days. The compound, after extracting with boiling alcohol and drying at 100°, forms glistening, bronzy crystals, and is only sparingly soluble in the usual solvents, but readily in chloroform. An alcoholic solution leaves dark green, rhombic crystals, which melt at 250—251° (uncorr.). When heated in a tube, it melts to a blue liquid, from which violet fumes of iodine are liberated. The iodine is readily removed from the molecule by warming with potash solution, by treatment with phenylhydrazine, or by nascent hydrogen. Warm acetic acid and mineral acids dissolve the compound, yielding yellowish-green fluorescent solutions. The author thinks that the compound is to be regarded as *tolyldi-iodoketoindene*,  $C_6H_4<\begin{matrix}CHI\\CO-\end{matrix}>CI\cdot C_6H_4Me$.

The product obtained by the action of dilute caustic soda on the above compound forms a red, amorphous powder, melts at 220°, and is probably *tolylketoindene*.

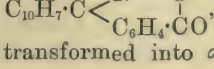
α-Naphthol does not react in the same manner. J. J. S.

**Derivatives of α-Naphthylamine.** By CARL BOETTINGER (*Chem. Zeit.*, 1895, **19**, 2080—2082; compare Abstr., 1895, i, 106).—A mixture of succino-α-naphthalide and succinonaphthil is obtained when succinic acid (1 mol.) is heated with α-naphthylamine (1½ mol.) in an oil bath at about 175°. The two are best separated by boiling alcohol. The α-naphthalide, $C_4H_4O_2(NH\cdot C_{10}H_7)_2$, is formed in small quantity; it is extremely sparingly soluble in boiling absolute alcohol, and melts at 275° (compare Hanamann, *Ber.*, 1877, **10**, 1713, who gives the melting point as 285°). It may be distilled in a vacuum without undergoing decomposition, and when heated with acetic anhydride in a sealed tube at 140°, it is partially converted into a *diacetyl* derivative, which melts at 122°.

*Succinonaphthil*, $C_4H_4O_2{:}NC_{10}H_7$, crystallises from aqueous alcohol in long prisms or compact tetrahedra, and melts at 151·5—153°; when warmed with alcoholic potash, it yields the potassium salt of α-naphthalidosuccinic acid (compare Hanamann).

Pyrotartaric acid reacts in very much the same way when heated with α-naphthylamine at 150°. The *dinaphthalide* of pyrotartaric acid is insoluble in ether, only sparingly soluble in boiling alcohol, and crystallises in long, colourless, hair-like needles, which melt at 243—244°. The corresponding *naphthil* is readily soluble in hot alcohol, forms colourless, compact crystals, and is decomposed by alcoholic soda into the sodium salt of the *naphthalido-acid*, which melts at 160—161°.

*Glycollic α-naphthalide*, $C_{12}H_{11}NO_2$, crystallises in colourless, four-sided plates, melts at 126—127°, and is insoluble in dilute soda. Tartaric α-naphthalide (compare Abstr., 1895, i, 106), when boiled for some time with acetic anhydride, yields a *tetracetyl* derivative, which crystallises in white needles, and melts at 243—244°. Neither the naphthalide nor its acetyl derivative are soluble in caustic soda solution. J. J. S.

**Synthesis of Chrysoketone (Naphthofluorenone) and the Constitution of Chrysene.** By CARL GRAEBE (*Ber.*, 1896, **29**, 826—828).—The naphthoylbenzoic acid, $C_{10}H_7\cdot CO\cdot C_6H_4\cdot COOH$, obtained from naphthalene and phthalic acid, must be an α-naphthalene derivative, for two reasons. First, it yields benzoic acid and α-, but no β-, naphthoic acid when fused with potash; and secondly, it yields an *oxime anhydride*,  $C_{10}H_7\cdot C<\begin{matrix}N\text{——}O\\C_6H_4\cdot CO\end{matrix}$, melting at 175—176°, which, when sublimed, is transformed into α-naphthylphthalimide,

$C_{10}H_7{\cdot}N<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$, melting at 181°, and the latter, when heated with hydrochloric acid at 130°, yields phthalic acid and $\alpha$-naphthylamine, but no $\beta$-naphthylamine. The amide of the acid, $C_{10}H_7{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, yields a yellow amine, $C_{10}H_7{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2$, melting at 140·5°; when this is diazotised, and the solution then warmed with water, a red substance, $CO<\begin{matrix}C_{10}H_6\\|\\C_6H_4\end{matrix}$, is formed, identical with the chrysoketone obtained by Bamberger and Kranzfeld from chrysene. It yields a yellow *oxime*, melting at 190°, and is reduced by hydriodic acid and phosphorus to chrysofluorene (which is better called naphthofluorene). All these substances are thus 1 : 2-naphthalene derivatives, and chrysofluorene has the formula $CH_2<\begin{matrix}C_{10}H_6\\|\\C_6H_4\end{matrix}$, chrysene having the formula, $\begin{matrix}CH{\cdot}C_{10}H_6\\ \|\qquad | \\ CH{\cdot}C_6H_4\end{matrix}$. This proof is held to be better than that deduced from the pyrogenic formation of chrysofluorene (Abstr., 1894, i, 337).

C. F. B.

**Acenaphtene [Acenaphthylene] Glycol.** By CARL GRAEBE and J. JEQUIER (*Annalen*, 1896, **290**, 205—206).—Ewan and Cohen obtained acenaphthylene glycol by hydrolysing the acetate arising from acenaphthylene bromide (Trans., 1889, 579); a more convenient method of preparation consists in treating the latter with boiling water. A readily soluble modification is produced along with the less soluble form, and melts at 145°; both are optically inactive, and are probably stereoisomeric.

M. O. F.

**Acenaphthenone.** By CARL GRAEBE and J. JEQUIER (*Annalen*, 1896, **290**, 195—204).—Acenaphthenone may be prepared from acenaphthene glycol by Ewan and Cohen's method (Trans., 1889, 580), or by reducing acenaphthenequinone (Abstr., 1893, i, 657); the last-named substance, when treated with phosphorus pentachloride, yields *dichloracenaphthenone*, which melts at 146·5°, and gives rise to acenaphthenone when treated with water at 150°. The *picrate* of acenaphthenone crystallises in yellow needles, and melts at 113°; the *phenylhydrazone* crystallises from alcohol, and melts at 90°. *Bromacenaphthenone* melts at 112°, and yields biacenaphthylidenediketone (*loc. cit.*) when treated with hot dilute caustic soda.

*Biacenaphthylidenone* (*dinaphthylenbutenone*), $\begin{matrix}CH_2-\\|\\C_{10}H_6\end{matrix}>C{:}C<\begin{matrix}CO\\|\\C_{10}H_6\end{matrix}$, is formed from acenaphthenone under the influence of alcoholic potash or acetic chloride, and crystallises from chloroform or benzene in yellow needles, being almost insoluble in alcohol; it melts at 262° (corr.). The ketone combines with two atomic proportions of bromine, yielding the *bromide*, which melts and decomposes at 280°.

*Benzylidenacenaphthenone*, $C_{10}H_6<\begin{matrix}C{:}CHPh\\|\\CO\end{matrix}$, is obtained by adding caustic soda to acenapthenone and benzaldehyde dissolved in alcohol; it melts at 107°, and the *oxime* melts at 48°.

M. O. F.

**Orientation in the Terpene Series: Pulegone.** By ADOLF VON BAEYER [and BERTRAM PRENTICE] (*Ber.*, 1896, **29**, 1078—1084; compare Abstr., 1895, i, 379).—Nitrosopulegone (*loc. cit.*) is a bisnitroso-derivative, differing, however, from members of this class in its property of yielding an oxime in addition to a dinitrosylic acid; this remarkable feature is explained by the fact that the bisnitroso-group $-NO_2N-$, is linked to the methylenic carbon, in juxtaposition to the ketonic group.

*Bisnitrosopulegone*, $(C_{10}H_{15}O)_2N_2O_2$, is obtained by adding hydrochloric acid to a mixture of pulegone, light petroleum, and amylic nitrite, cooled with melting ice. Caustic soda converts it into *isonitrosopulegone*, $C_{10}H_{15}NO_2$, which crystallises in straw-yellow needles, and decomposes at 122—127°; *pulegonedioxime hydrate*, $C_{10}H_{18}N_2O_3$, is produced by the action of hydroxylamine on isonitrosopulegone.

*Pulegonedinitrosylic acid*, $C_{10}H_{16}N_2O_3$, is obtained by the action of hydrogen chloride on an ethereal solution of bisnitrosopulegone; it crystallises from light petroleum in slender, colourless needles, and melts at 115—116°.

Along with bisnitrosopulegone, there are formed 2-*chloropulegone*, which crystallises in long needles, and melts at 124—125°, and *di-isonitrosomethylcyclohexanone*, the formation of which depends on the elimination of the $C_3H_6$ group; its empirical formula is $C_7H_{10}N_2O_3$, and it decomposes at 190°; the *diacetate* melts at 125—130°. The *anhydride* of tri-isonitrosomethylcyclohexanone, $C_7H_9N_3O_2$, obtained by the action of hydroxylamine, melts at 128—129°; the *acetate* of the anhydride melts at 139—140°. M. O. F.

**Partial Synthesis of Geranic acid. Constitution of Lemonol [Geraniol] and Lemonaldehyde [Geranaldehyde].** By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 393—395).—Since methylheptenonecarboxylic acid and terebic acid are found only in small quantities when lemonaldehyde is oxidised, it seems most probable that they are really derived from impurities. When natural methylheptenone is condensed with ethylic iodoacetate in presence of zinc, and the product is decomposed by water, a colourless oil of the composition $C_{10}H_{17}O_3Et$ is obtained, which boils at 125—135°, under a pressure of 7 mm., and yields an acetate which boils at about 140°, under a pressure of 7 mm., and at 250° under ordinary pressure. If the acid $C_{10}H_{18}O_3$ is boiled with acetic anhydride, it is converted into geranic acid, and if the ethereal salt, $C_{10}H_{17}O_3Et$, or the corresponding acetate, is boiled with acetic acid containing some zinc chloride, ethylic geranate is obtained.

This partial synthesis of geranic acid establishes Tiemann's formula for geranaldehyde, $CHO{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$, and necessitates revision of the formulæ proposed by the authors for licareol and licarhodol. C. H. B.

**Extraction of Rhodinol from Oil of Pelargonium and from Oil of Roses. The Identity of these two Products.** By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 529—531; compare Abstr., 1895, i, 78).—The authors are convinced as to the difference between rhodinol and geraniol, a difference recently called in question by Erdmann and Huth (this vol., i, 198).

The product extracted from oil of pelargonium contains some geraniol, together with a second alcohol. By treating the extract with benzoic chloride, the geraniol is decomposed, and, on distillation, a benzoate is found in the fraction passing over between 180° and 220° (10 mm.). This, on hydrolysis with alcoholic potash, yields a colourless, agreeably smelling liquid, of the formula $C_{10}H_{20}O$, and boiling at 110° (10 mm.).

For this substance, the authors propose the name rhodinol; its sp. gr. = 0·8731 at 0°, and its rotation $\alpha_a = -2° 11'$. Its *acetate* is a colourless, agreeably smelling liquid, boiling at 115° (10 mm.).

That portion of oil of roses boiling at 110—115° (10 mm.), on treatment in the same manner, yields an alcohol having the same boiling point and specific gravity, being also lævorotatory to the same extent. The authors consider the two substances to be identical. Rhodinol occurs in these oils only to the extent of about 20 per cent. J. F. T.

**Constitution of Rhodinol.** By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 673—675).—Rhodinol (Abstr., 1895, i, 78), when oxidised with chromic mixture, yields (*a*) *rhodinaldehyde*, $C_{10}H_{18}O$, which boils at 90° under a pressure of 10 mm., and is under investigation; (*b*) *rhodinic acid*, $C_9H_{17}\cdot COOH$, an oily liquid, with a powerful and disagreeable odour. It boils at 147° under a pressure of 10 mm., and is identical with the acid obtained by the oxidation of rhodinol from oil of pelargonium, to which the composition $C_{10}H_{16}O_2$ was erroneously attributed (*loc. cit.*); (*c*) *rhodinylic rhodinate*, $C_{20}H_{36}O_2$, a neutral oil, which has a disagreeable odour, and boils at 190°, under a pressure of 10 mm.

Acetone and $\beta$-methyladipic acid are also formed. The acid previously described as $\alpha$-methyladipic acid (*loc. cit.*) is really the $\beta$-modification.

Rhodinol from roses yields similar results, and it follows that rhodinol is a primary open-chain alcohol, with one ethylenic function, and its constitution is most probably

$$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH,$$

or $CMe_2{:}CH\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$. C. H. B.

**Sobrerol ($\Delta$-Menthene-2 : 8-diol).** By ALEXANDER GINZBERG (*Ber.*, 1896, **29**, 1195—1198).—When sobrerol is oxidised by potassium permanganate, the tetrahydric alcohol, *sobreritritol*, $C_{10}H_{20}O_4$, is produced (Wagner, Abstr., 1894, i, 470); this substance is excessively hygroscopic, owing to its tendency to form the *hydrate*, $C_{10}H_{20}O_4 + 2H_2O$, which separates from water in monoclinic crystals, and melts at 100—105°, losing water at 120°, after which it melts at 155·5—156°. Oxidation of sobreritritol with potassium permangagate yields acetic and terebic acids, the main product being terpenylic acid; from this it follows that the alcohol in question is menthane-

1 : 2 : 6 : 8-tetrol, whilst sobrerol, formed from pinol by rupture of the oxide bond, is $\Delta^6$-menthene-2 : 8-diol, or $\Delta^1$-menthene-6 : 8-diol.

Contrary to the statement of Wallach, sobrerol, when treated with boiling acetic anhydride, yields the *diacetate*, a bitter, viscous liquid of agreeable odour, having the sp. gr. = 1·0385 at 18°.

M. O. F.

**Dehydration of Menthane-1 : 2 : 8-triol.** By ALEXANDER GINZBERG (*Ber.*, 1896, **29**, 1198—1202).—Trihydroxymenthane yields cymene and the *diacetate* of a glycol when heated for six hours with acetic anhydride (3 mols.) at 150°; the *glycol*, $C_{10}H_{18}O_2$, isomeric with sobrerol, separates from light petroleum in colourless, triclinic prisms, melts at 63—64°, and boils at 259—260° under a pressure of 754 mm. Oxidation with potassium permanganate converts it into a tetrahydric *alcohol*, $C_{10}H_{20}O_4$, identical in crystalline form with the limonetritol of Morosewitz and Wulf; it is, however, optically inactive, and melts at 168·5—169·5°.

The new glycol, which is most probably $\Delta^{8(9)}$-*menthene*-1 : 2-*diol*, is not formed when acetic chloride acts on trihydroxymenthane, the products being sobrerol and cymene. M. O. F.

**Laurolene, a Hydrocarbon of the Camphor Group.** By OSSIAN ASCHAN (*Annalen*, 1896, **290**, 185—194).—*Laurolene*, $C_8H_{14}$, is obtained by slowly distilling camphanic acid in an atmosphere of carbonic anhydride, the yield amounting to 50 per cent. when the operation is conducted at the rate of about 10 drops a minute; if the distillation is carried on more rapidly, a considerable quantity of lauranolic acid is produced (Abstr., 1895, i, 154). Laurolene boils at 119° (uncorr.), has the sp. gr. = 0·80187 at 18·6°/4°, and the specific rotatory power $[\alpha]_j = -23·0°$; the refractive index $n_D = 1·4479$ at 18°, whence the molecular refraction M = 36·70°, the value calculated for one ethylenic linking being 36·43. The hydrocarbon reduces a cold, alkaline solution of potassium permanganate, and combines with two atomic proportions of bromine; its behaviour towards sulphuric and nitric acids, potassium ferricyanide, and potassium permanganate is inconsistent with the presence of a ring containing 6 atoms of carbon. M. O. F.

**Camphorone, Isophorone, and Mesitylic Oxide.** By WILHELM KERP (*Annalen*, 1896, **290**, 123—152).—The author has submitted camphorone to a detailed comparison with phorone obtained by the condensation of acetone, and shows that these substances, although isomeric, are not identical (compare Abstr., 1892, 626); reference is now made to the latter compound as isophorone.

*Isophorone*, $C_9H_{14}O$, is obtained by the action of sodium ethoxide on acetone, the yield amounting to 7 or 8 per cent.; it boils at 100—102° under a pressure of 15 mm., and the sp. gr. = 0·9255 at 20·5°/4°. When the substance is reduced by adding water to the ethereal solution containing sodium, an *alcohol*, $C_9H_{18}O$, which melts at 37°, and boils at 87° under a pressure of 15 mm., is formed along with the *pinacone*, $C_{18}H_{34}O_2$, which melts at 155°. *Isophoroneoxime* crystallises in transparent prisms, and melts at 79—80°; it is indifferent towards concentrated sulphuric acid and zinc chloride, and, on reduction with sodium and alcohol, yields the *base* $C_9H_{15}\cdot NH_2$, which boils at 81—85°, forms the *oxalate* melting at 224—225°, and the *carbamide* derivative, which crystallises in white needles and melts at 185°. When isophorone is oxidised with potassium permanganate, formic and acetic acids are among the products, also an *acid* of the formula $C_8H_{14}O_4$.

Camphorone, on reduction, yields the *alcohol* $C_9H_{16}O$, which boils at 77—81° under a pressure of 16 mm., and the *pinacone* $C_{18}H_{30}O_2$, which sinters at 135—140°, and melts at 160—162°. Camphorone-oxime (Abstr., 1893, i, 361) contains $1H_2O$, and, on reduction, yields a base which probably has the formula $OH\cdot C_9H_{16}\cdot NH_2$; the *oxalate* is crystalline.

Camphorone, isophorone, and crystallised acetophorone all yield pseudocumene when they are distilled with phosphoric anhydride; the first-named also gives rise to cumene, whilst acetophorone yields mesitylene.

Reduction of mesitylic oxide converts it into methylisobutylcarbinol. The oxime yields β-isohexylamine and hydroxy-β-isohexylamine.

*β-Isohexylamine*, $C_6H_{15}N$, is a limpid base of ammoniacal odour which absorbs atmospheric carbonic anhydride, and boils at 100—103°; the *hydrochloride* and *platinochloride* are well defined, the *oxalate* melts at 219°, and the *carbamide* derivative at 139·5—140°.

*Hydroxy-β-isohexylamine*, $OH\cdot C_6H_{12}\cdot NH_2$, has a feebly ammoniacal odour, and boils at 171—174°; the *oxalate* melts at 206°.

The *hydrocarbon* $C_6H_{10}$ is produced along with the foregoing bases, and boils at 77—78°; the *tribromo-compound*, $C_6H_9Br_3$, is an oil.

M. O. F.

### Conversion of Dextrocamphoric acid into Dextrocamphor.

By Albin Haller (*Compt. rend.*, 1896, **122**, 446—449).—When campholide is heated with potassium cyanide in sealed tubes at 230—240°, it yields cyanocampholic acid, identical with that obtained from cyanocamphor, and this acid, when heated with potassium hydroxide, yields bromocamphoric acid, identical with that prepared from cyanocamphor. The lead salt of this bromocamphoric acid, when heated, yields camphor identical in all its properties with ordinary camphor.

These results show (1) which part of the molecule is oxidised in the conversion of camphor into camphoric acid, (2) that the fundamental nucleus to which camphor owes its rotatory power is not destroyed by conversion into camphoric acid, campholide, cyanocampholic acid, or bromocamphoric acid. They are also in accordance with the view that the camphoric and bromocamphoric acids have a double carboxylic function.

C. H. B.

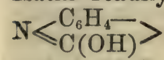
### Russian Oil of Anise.

By Gustave Bouchardat and Tardy (*Compt, rend.*, 1896, **122**, 624—626).—The commercial oil contains a large proportion of anethoïl, $C_{20}H_{12}O_3$, a very small quantity of anisaldehyde, anisic acetone, $C_{20}H_{10}O_4$, anisic acid, and anethoïl, fenchone, $C_{20}H_{16}O_2$, and also some hydrocarbons of the formula $C_{30}H_{24}$. No new compounds are described in this paper. J. F. T.

**Euxanthone.** By F. MANN and BERNHARD TOLLENS (*Annalen*, 1896, **290**, 159—164).—The *disodium* and *dipotassium* derivatives are crystalline, and the *calcium* derivative is obtained as a gelatinous precipitate on adding a solution of calcium chloride to euxanthone dissolved in ammonia and alcohol; the *barium* derivative separates from dilute alcohol in red crystals.

When euxanthone is reduced with sodium amalgam, the *compound* $C_{26}H_{18}O_7$ is obtained, separating from alcohol in dark violet crusts; the solution in concentrated hydrochloric acid is red, the absorption spectrum exhibiting a band almost coincident with the D line.

M. O. F.

**Isatin.** By LEO MARCHLEWSKI (*Ber.*, 1896, **29**, 1030—1034).—Isatin readily reacts with semicarbazide to form a *semicarbazone*,  $N{<}\begin{smallmatrix}C_6H_4—\\C(OH)\end{smallmatrix}{>}C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, which crystallises in yellow needles, melts and decomposes at about 260°, and dissolves in strong aqueous soda and strong acids, but not in dilute acids. *Parachlorisatinsemicarbazone* crystallises in stellate groups of light yellow needles, and is more strongly acid than isatinsemicarbazone. It becomes brown at about 230°. *Nitroisatinsemicarbazone* crystallises in slender, pale yellow needles. Isatin and its derivatives, therefore, act as monoketones towards semicarbazide. A. H.

**Carbostyril and its Derivatives: Tautomerism.** By ADOLPH CLAUS (*J. pr. Chem.*, 1896, [2], **53**, 325—334).—The bromination of carbostyril leads to the conclusion that it exists in tautomeric forms, and the author develops the theory which he has previously outlined (Abstr., 1895, i, 257) in this connection. The subject of tautomerism must now be considered from three points of view, namely, that of the "central" linking theory (*loc. cit.*), that of the existence of racemic forms, and that of continually changing bonds.

A. G. B.

**4-Hydroxyquinoline.** By ADOLPH CLAUS (*J. pr. Chem.*, 1896, [2], **53**, 335—339; compare Abstr., 1893, i, 484; this vol., i, 255).—When 4-hydroxyquinoline and bromine, in molecular proportion, are brought together in glacial acetic acid, a yellow, crystalline precipitate is formed, consisting of a mixture of the hydrobromides of 4-hydroxyquinoline, 1 : 4-bromohydroxyquinoline, and 1 : 3 : 4-dibromohydroxyquinoline. To separate these, the aqueous solution of the precipitate is much diluted, whereby the dibromo-derivative, being a very feeble base, is thrown down; the bromo-derivative may then be precipitated by the addition of sodium acetate.

1 : 4-*Bromohydroxyquinoline* darkens at 165—170°, and melts at about 190°. 1 : 3 : 4-*Dibromohydroxyquinoline* begins to decompose at 130—140°, and does not melt at 300°.

3 : 4-*Bromohydroxyquinoline* crystallises in yellowish needles, and melts at 162°.

4 : 1-*Hydroxyquinolinesulphonic acid* is obtained by sulphonating 4-hydroxyquinoline in the usual manner; it crystallises, when hydrochloric acid is added to the hot solution of its sodium salt, in lustrous, yellow prisms, with $1H_2O$, and melts at about 300°; it is only very slightly soluble in neutral solvents; its *sodium* salt forms hard, brilliant, dark red prisms with $1H_2O$. A. G. B.

**Reactions of Salts of Alkaloïds with various Indicators.** By H. W. Salomonson (*Chem. Centr.*, 1895, ii, 536, 826; from *Ned. Tydschr. Pharm.*, **7**, 195—203; 225—234).—The author has found that quinine is a dibasic alkaloïd, and that the compound of 1 mol. of quinine with 2 mols. of hydrogen chloride must therefore be considered as the normal salt. If this salt were of an acid nature, it would not be neutral to methyl-orange; it is, however, acid to litmus.

When titrating salts of quinine, good results are obtained by the use (1) of indicators which are not acted on by the liberated alkaloïd until the last trace of acid has been neutralised; for example, phenolphthaleïn; (2) of indicators such as rosolic acid, and litmus, which are affected not by the free alkaloïd, but by its basic salts; (3) of indicators such as methyl-orange, which are only dissociated by perfectly neutral salts. L. de K.

**Isolation of Adenine from Tea Extract.** By Martin Krüger (*Zeit. Physiol. Chem.*, 1895, **21**, 4, 274—284).—Of the methods for isolating adenine (1) by ammoniacal silver nitrate, and (2) by copper sulphate and sodium hydrogen sulphite, direct comparison shows the latter to be the better.

The adenine precipitated by the former method is accompanied by a second *substance* which may be obtained from the mother liquors. It crystallises in delicate, silky prisms, and dissolves readily in hot water, less readily in cold. From its aqueous solution, picric acid precipitates adenine picrate, whilst theobromine occurs in the mother liquor. The substance is, therefore, a compound of adenine and theobromine, $C_5H_5N,C_7H_8N_4O_2$, and may be obtained by dissolving molecular proportions of its constituents in hot water, when it separates in delicate white needles. On recrystallisation from water, it is decomposed, theobromine being deposited.

A third *substance* occurring in the above silver precipitate is isolated after precipitating the adenine by means of picric acid from the mixture of free bases. The mother liquors are freed from picric acid by acidification and extraction with ether, the bases being then precipitated by ammoniacal silver nitrate. The precipitate is recrystallised from dilute nitric acid, the less soluble portions being collected and decomposed in hot water by hydrogen sulphide, the filtered liquid being then boiled and rendered alkaline by ammonia. The new base is precipitated in aggregates of long, slender, needles, and dissolves somewhat readily in hot water; on treatment with concentrated nitric acid, a dark yellow substance is left which becomes a brilliant red with gaseous ammonia or sodium hydroxide; when acted on by a mixture of hydrochloric acid and potassium chlorate, and then with gaseous ammonia, a violet-red coloration is produced. It dissolves in 33 per cent. caustic soda, and, with picric acid, gives yellow needles soluble in water. The *hydrochloride* is sparingly soluble in hydrochloric acid, and forms shining, colourless needles; the *nitrate* forms compact, facetted, lustrous crystals; the *platinochloride* crystallises in brilliant, four-sided, orange-red prisms, and the *aurochloride* in fern-like, skeleton forms.

Hypoxanthine does not occur in tea extract, but is probably produced from the silver derivative of adenine by the oxidising action of the nitric acid from which it is usually crystallised, hence the statements as to its presence. A. L.

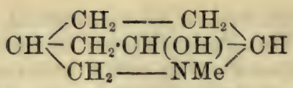
**Pseudaconitine.** By MARTIN FREUND and ROBERT NIEDERHOFHEIM (*Ber.*, 1896, **29**, 852—858).—The pseudaconitine investigated by the authors melted at 212°, whilst the melting point is stated to be 104—105° by Wright (Trans., 1878, 151), and 201° by Dunstan and Carr (Proc., 1895, 154). The *hydriodide*, $C_{36}H_{49}NO_{12},HI$, crystallises in prisms, and melts at 215—217°. The *aurochloride* melts at 236—238°, whilst the *nitrate* crystallises in thin prisms or plates which melt and decompose at 185—186°, and the *thiocyanate* decomposes at 195—200°.

When the base is boiled with water, it yields acetic acid and *picropseudaconitine*, $C_{34}H_{47}NO_{11}$, which forms compact crystals melting at 210°; a fact previously established by Dunstan and Carr (*loc. cit.*), who, however, give the m. p. as 181°. The *hydriodide* crystallises in prisms which melt and decompose at 205—207°. No crystalline nitrate could be obtained. When picropseudaconitine is boiled with strong aqueous potash, it yields veratric acid and *pseudaconine*, $C_{25}H_{39}NO_8$, to which Wright gave the formula $C_{27}H_{41}NO_9$. It is a yellowish-brown, amorphous mass, but yields a crystalline *acetone compound*, $C_{25}H_{39}NO_8 + C_3H_6O$, which melts at 86—87°, and dissolves in water, forming a solution which leaves the amorphous pseudaconine when evaporated. It crystallises in hemihedral forms of the rhombic system, the crystallographic constants being $a : b : c = 0·95462 : 1 : 1·3735$.

These results make it probable that pseudaconitine is acetylveratroylanhydro-aconine, $C_6H_3(OMe)_2·CO·C_{25}H_{37}NO_8·Ac$. A. H.

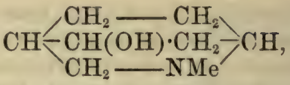
*Note.*—Most of the facts in the above paper have been already published by Dunstan and Carr in a preliminary communication to this Society (Proc., 1895, 154), in which they stated that they were still engaged in this investigation.—EDITORS.

**Ketones of the Tropine-group II.—ψ-Tropine.** By RICHARD WILLSTÄTTER (*Ber.*, 1896, **29**, 936—947).—The preparation of tropinone from tropine has been previously described (this vol., i, 327). When reduced by means of sodium in moist ethereal or alcoholic solution, or by sodium amalgam in dilute hydrochloric acid solution, tropinone is converted into ψ-tropine, which was fully identified by the preparation of numerous derivatives; when oxidised, tropinone is regenerated. Tropine is readily converted into ψ-tropine by heating with sodium amyloxide in amylic alcoholic solution; these results show that the compounds are not structurally isomeric,



$$\mathrm{CH}\left\langle\begin{array}{l}\mathrm{CH_2}\text{——}\mathrm{CH_2} \\ \mathrm{CH_2{\cdot}CH(OH)} \\ \mathrm{CH_2}\text{——}\mathrm{NMe}\end{array}\right\rangle\mathrm{CH}$$

and



$$\mathrm{CH}\left\langle\begin{array}{l}\mathrm{CH_2}\text{——}\mathrm{CH_2} \\ \mathrm{CH(OH){\cdot}CH_2} \\ \mathrm{CH_2}\text{——}\mathrm{NMe}\end{array}\right\rangle\mathrm{CH},$$

as Liebermann suggested. Both are optically inactive, and contain three asymmetric carbon atoms (see below); three cases of geometrical isomerism are discussed.

(1) *Isomerism of Cyclohexane.*—Sachse (Abstr., 1890, 1386) has shown that cyclohexane and its derivatives might exist in two forms, but no experimental verification of this has been given, and no isomeric hexahydrobenzoic acid is known; v. Baeyer's present view is that the carbon atoms in cyclohexane, as in the other polymethylenes, are in one plane, and that the cause of *cis-trans*-isomerism lies in their occupying a middle position of greatest stability.

(2) *Isomerism as in the case of Piperidine Derivatives.*—This has been discussed by Ladenburg (Abstr., 1893, i, 442; and 1894, i, 306), but lacks experimental proof.

(3) *Isomerism due to the Double Ring containing Nitrogen.*—Until the geometrical isomerism occurring in double ring compounds, such as borneol derivatives, and in cyclic nitrogen compounds, such as the monosubstitution products of piperidine, has been fully investigated, the discussion of this form of geometrical isomerism would be premature.

The author inclines to the belief that the relationship of tropine and ψ-tropine is an instance of *cis-trans*-isomerism due to the relative position in space of the methyl and hydroxyl groups.

Ladenburg has suggested (*Ber.*, 1896, **29**, 424) that tropinone is an aldehyde, and has pointed out that its production accords as well with his as with Merling's tropine formula. The subject is being further investigated, but the production of tropinic acid from dihydroxytropidine, and its resolution into adipic acid is against Ladenburg's view.

Tropinone is very readily reduced by sodium in boiling alcoholic solution, or by means of sodium amalgam (see above); the yield of ψ-tropine is quantitative, and no tropine could be detected, even traces. *Benzoyl-ψ-tropeine*, prepared by Liebermann's method from ψ-tropine, is identical with tropacocaïne contained in Java coca leaves, and is the first example of the conversion of an alkaloïd of the Solanaceæ into one of the Erythroxyleæ (coca), and it affords confirmation of the relationship which has been shown to exist between the cocaïne and atropine groups. The *nitrate* and *picrate* are sparingly soluble; the *hydrobromide* crystallises in silky, lustrous plates; the *hydrochloride* in highly refractive, rhombic plates melting and decomposing at 270°. The *mercurochloride* is crystalline; the *platinochloride* is deposited in pale, slender needles; the *aurochloride* crystallises in needles melting and decomposing at 207—208°. The yield of ψ-tropine, boiling within three degrees, prepared directly from tropine, is 75 per cent. of the theoretical, that of the purified product is 50—55 per cent. Attempts to regenerate tropine from ψ-tropine by the action of sulphuric acid at the ordinary temperature were unsuccessful.

J. B. T.

**A New Enzyme from Yeast.** By A. BAU (*Chem. Zeit.*, 1895, **19**, 1873—1874).—Melitriose, when treated with an invertase solution, is hydrolysed to melibiose and a monose (probably fructose), both of which the author has isolated in the form of their osazones. It is stated that yeast, dried at such a temperature as not to destroy the enzymes, and then digested with water, yields no sugar, whereas Salkowski states that fresh yeast when digested with water yields fructose.

A melibiose solution when digested with dried top yeast is not acted on, but with dried bottom yeast (Frohberg type) it is completely converted into glucose and galactose. A mixture of the two yeasts also brings about the same decomposition. The enzyme which is present in the bottom yeast and which brings about this decomposition, the author terms *melibiase*.

Thus in yeast (so-called *Saccharomyces cerevisiæ*) the following enzymes are present: (1) Invertase, or, as the author prefers to term it, *eninvertase*, this is soluble in water, is precipitated by alcohol and decomposes cane sugar into glucose and fructose, and melitriose into fructose and melibiose; (2) yeast glucase (compare C. J. Lintner and Emil Fischer), which is insoluble in water, and which decomposes maltose and isomaltose into glucose; (3) melibiase, also insoluble in water. J. J. S.

**Constitution of Cholic acid.** By MICHAEL SEŇKOWSKI (*Monatsh.*, 1896, **17**, 1—3).—Cholic acid behaves towards halogens as a saturated compound. It is oxidised by alkaline permanganate, the resulting mixture of acids yielding, on distillation with steam, acetic and propionic acids but no benzoic acid; the non-volatile portion when extracted with ether, yields some impure phthalic acid.

A. L.

**Specific Rotation of Cholic acid, Choleic acid, and Deoxycholic acid.** By E. VAHLEN (*Zeit. physiol. Chem.*, 1895, **21**, 4, 253—273).—Cholic acid is most readily purified by preparing its potassium salt, dissolving the latter in dilute alcohol, and precipitating it with a mixture of absolute alcohol and ether, the crystalline precipitate being washed with the same mixture; the last traces of colouring matter may be removed by exposing the acid to sunlight. Crystals of the acid from acetic acid and hot alcohol melt at 180—187° (not 185—187°).

Determinations of the rotatory power of cholic acid made (1) with specimens containing 1 mol. of alcohol of crystallisation, gave $[\alpha]_D = 35\cdot11$; (2) with specimens of pure acid, gave $[\alpha]_D = 37\cdot02$. The high value $[\alpha]_D = 49\cdot4$ obtained by Hoppe Seyler (*J. pr. Chem.*, 1863, **2**, 257) from direct observation on solutions of the dry acid were certainly due to impurity. Potassium cholate in aqueous solution gave values of $[\alpha]_D = 26\cdot66—31\cdot35$, whence the deduced values for free cholic acid are $[\alpha]_D = 29\cdot22—34\cdot35$; in alcoholic solution the salt has the rotation $[\alpha]_D = 31\cdot27—31\cdot59$, whence for free cholic acid, $[\alpha]_D = 34\cdot26$. Sodium cholate in aqueous solution gave numbers making $[\alpha]_D = 27\cdot45—30\cdot61$, giving for free cholic acid

$[\alpha]_D = 29{\cdot}03$—$32{\cdot}37$. The mean molecular rotations of the potassium and sodium salts are practically identical.

Dextrorotatory choleic acid in aqueous solution has a specific rotation $[\alpha]_D = +48{\cdot}60$—$52{\cdot}48$.

The rotations of the above substances were found to be considerably affected by the concentration and temperature of the solutions.

Deoxycholic acid, prepared according to Mylius's directions from putrefying ox-gall, melted at 153—155° (not 160—170°), and had in alcoholic solution the specific rotation $[\alpha]_D = +49{\cdot}86$. A. L.

**Proteïds of the Kidney Bean (Phaseolus Vulgaris).** By Thomas B. Osborne (*J. Amer. Chem. Soc.*, 1894, **16**, 633—643 and 703—712).—The author confirms most of the work previously done by Ritthausen (*J. pr. Chem.*, **103**, 204, and [2], **29**, 452), but states that the aqueous extract of the bean is always distinctly acid, and also, in opposition to Ritthausen, that a 5 per cent. saline solution extracts a proteïd from the crushed beans.

The author has been enabled to identify and obtain in a state of comparative purity two distinct proteïds, one, the more abundant, having the properties of a globulin, which he designates *phaseolin*, and another, not so definite in character, which he terms *phaselin.*

The phaseolin is best obtained by extracting freshly ground bean meal, which has been treated with ether, with sodium chloride solutions (1—10 per cent.), and then precipitating with water, ammonium sulphate, or dilute acids. The precipitate, after filtration for 24 hours, and after dialysis for about six days in river water, consists of nearly pure phaseolin. That it really consists of a single proteïd has been shown by repeated fractional precipitation; each fraction was found to give practically the same results, on analysis. The amount of proteïd extracted by a sodium chloride solution is about 15 per cent. of the seed. Water is found to extract about 11 per cent. of the same proteïd. The phaseolin was obtained in the form of well-formed tetrahedral crystals by taking the clear extract obtained by a 1 per cent. sodium chloride solution and dialysing in a large vessel containing alcohol. The analysis of the purest sample obtained by repeated solution and precipitation gave $C = 52{\cdot}49$, $H = 6{\cdot}90$, $N = 16{\cdot}46$, $S = 0{\cdot}50$, ash $= 0{\cdot}69$.

It is entirely insoluble in cold or warm distilled water, but readily dissolves in sodium chloride solution and in very dilute acids and alkalis, yielding a clear solution. Acetic, hydrochloric, nitric, and sulphuric acids do not precipitate the proteïd from its 10 per cent. sodium chloride solution, but it is precipitated from its 1 per cent. sodium chloride solution by means of dilute hydrochloric acid. Solutions of the proteïd in brine are all precipitated by ammonium sulphate, or by a mixture of potassium ferrocyanide and acetic acid.

A violet colour is obtained with copper sulphate and potash, and with nitric acid, the xanthoproteïc reaction is given.

No turbidity occurs in the 2 per cent. sodium chloride solution until the temperature reaches 95°, and at 100°, a small quantity of a flocculent precipitate is formed. In composition, it resembles the myosins found in maize and oats (Abstr., 1891, 1390).

The second proteïd, *phaselin*, remains in solution after the phaseolin has been precipitated, and may be separated by dialysis in distilled water, by adding acids, and by prolonged heating. The proteïd obtained by any of these means has nearly the same composition. The purest specimen gave C = 49·01, H = 6·77, N = 14·04, ash = 4·58 per cent. When dried over sulphuric acid, it is almost wholly soluble in water, but, after drying at 110°, it becomes insoluble.

J. J. S.

**The Proteïds of Barley.** By THOMAS B. OSBORNE (*J. Amer. Chem. Soc.*, 1895, **17**, 539—567).—The proteïds, which are soluble in water, the author shows to be leucosin and proteose (compare this vol., i, 399), and the proteïd soluble in sodium chloride solution is edestin (this vol., i, 400). Another proteïd, however, occurs in barley meal; this is soluble in dilute alcohol (75 per cent.), and the author designates it *hordein.* This hordein is apparently the same proteïd as that described by Kreusler; it resembles gliadin in many of its properties, but differs from it considerably in composition; hordein contains 1½ per cent. more carbon, 1½ per cent. less nitrogen, and 0·3 per cent. less sulphur than gliadin. When completely dried at 110°, hordein is almost insoluble in water; the dilute solutions, which can be obtained by means of hot water, do not precipitate on cooling, or coagulate on boiling, but yield a precipitate on the addition of salt. It is also soluble in very dilute alkalis and acids, but is thrown down again on neutralisation. Dissolved in concentrated hydrochloric acid, a beautiful, crimson colour is produced, and a warm mixture of equal volumes of water and concentrated sulphuric acid gives a red colour with hordein, not a purple-red, as with gliadin.

Barley also contains a proteïd, insoluble in water, saline solutions, and alcohol, but soluble in potash. It was not found possible to isolate this compound in a state of purity.

The amounts of the various proteïds present are, globulin (edestin) and proteose, 1·95 per cent.; leucosin, 0·3 per cent.; hordein, 4 per cent.; and insoluble proteïd, 4·5 per cent. J. J. S.

**Deamidation of Glutin-Peptone.** By CARL PAAL (*Ber.*, 1896, **29**, 1084—1085; compare Abstr., 1894, 559).—When nitrous acid acts on glutin-peptone, nitrogen is eliminated, and a nitrosamine is produced; this indicates the existence of an imido-group along with amido-nitrogen in the original substance, which also contains tertiary nitrogen, because the nitrosamine in question has basic properties.

*Deamidonitrosoglutin-peptone* is obtained by carefully adding silver nitrite suspended in water to a solution of glutin-peptone hydrochloride in hot water, the operation being finished when dissolved silver appears in the liquid; silver chloride having been removed by filtration, the solution is treated with hydrogen sulphide until nitrous acid is no longer present, filtered from silver sulphide, and extracted with ether in order to remove an oily bye-product. The aqueous solution is then evaporated, and the residual syrup poured into absolute alcohol, which precipitates the amorphous peptone derivative; the alcoholic solution deposits it as a yellow, brittle, vesicular mass, which is very hygroscopic, and dissolves most readily in water, being sparingly soluble in hot, absolute methylic alcohol. The substance gives the biuret reaction, and is precipitated by phosphotungstic acid in alkaline or acid solution; concentrated sulphuric acid eliminates the nitroso-group in the form of nitrous acid.

When treated with much ether, the filtrate from the precipitate of deamidonitrosopeptone obtained on pouring the aqueous syrup into absolute alcohol, yields a substance which the author calls *deamidonitrosopropeptone*, giving the biuret reaction, and being precipitated by phosphotungstic acid. These two new compounds have been obtained from three distinct preparations of glutin-peptone, and details are given regarding the production and properties of their *hydrochlorides.*

*Deamidoglutin-peptone* is formed from deamidonitrosopeptone on eliminating the nitroso-group by reduction with zinc and dilute sulphuric acid; it is thus obtained as a pale yellow, hygroscopic mass, which dissolves sparingly in hot ethylic alcohol. The substance gives the biuret reaction, and is precipitated by phosphotungstic acid. The *hydrochloride* is a yellow, hygroscopic mass. M. O. F.

**Mucin of Connective Tissue.** By RUSSELL H. CHITTENDEN and WILLIAM J. GIES (*J. Exper. Med.*, 1896, **1**, 188—201).—Mucin prepared from tendons by precipitating the lime water extract of them with hydrochloric acid, gave the following percentages on elementary analysis.

| | 1. | 2. | 3. | Loebisch's average (Abstr., 1886, 166). |
|---|---|---|---|---|
| C | 49·29 | 48·74 | 48·26 | 48·30 |
| H | 6·63 | 6·46 | 6·49 | 6·44 |
| N | 11·94 | 11·80 | 11·51 | 11·75 |
| S | 2·34 | 2·35 | 2·31 | 0·81 |
| O | 29·80 | 30·65 | 31·43 | 32·70 |

No. 3 is regarded as the purest preparation and the results agree closely with those of Loebisch, except in the percentage of sulphur. There is, however, probably more then one mucin in connective tissue, and the sulphur may be largely due to admixture with proteïd matter. Preliminary extraction of the tissue with 10 per cent. sodium chloride solution is the best way to get rid of this. This was done in the case of preparation 3.

The reactions of mucin are well given by Loebisch. From the carbohydrate which can be cleaved off from it, a crystalline osazone was prepared, melting at 160°. It appears to resemble very closely that obtained by Hammarsten from the nucleo-proteïd of the pancreas (Abstr., 1894, i, 310). W. D. H.

# Organic Chemistry.

**Conversion of Trimethylene into Propylene.** By SIMEON M TANATAR (*Ber.*, 1896, **29**, 1297—1300).—When trimethylene is passed slowly through a glass tube heated to a dull red heat in a combustion furnace, the product is absorbed, for the most part, by cooled sulphuric acid, and from the resulting solution isopropylic (and propylic) alcohols can be isolated. A conversion of trimethylene into its isomeride, propylene, must have taken place in the tube; this corresponds with a loss of energy (7·7 Calories), and is analogous to the conversion of maleïc into fumaric acid. C. F. B.

**Preparation of Diethylenic Hydrocarbons.** By H. FOURNIER (*Bull. Soc. Chim.*, 1895, [3], **13**, 882—884).—The author describes certain hydrocarbons produced by the elimination of the elements of water from the secondary alcohols previously described by him (Abstr., 1894, i, 19, 394; 1895, i, 198). The alcohol is heated in an oil bath at 120°, with three times its weight of potassium hydrogen sulphate for some time. The hydrocarbon is then distilled over, and purified by fractionation.

*Methyl*-6-*heptandiene*-1 : 3, $CHMe_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH{:}CH_2$, is prepared from isobutylallylcarbinol; it boils at 115—117°, and its sp. gr. = 0·741 at 22°.

*Decandiene*-1 : 3, $C_6H_{13}{\cdot}CH{:}CH{\cdot}CH{:}CH_2$ ?, is formed from hexylallylcarbinol. It is a colourless liquid boiling at 168—170°, and having a sp. gr. = 0·750 at 20°. J. F. T.

**Preparation of Allylene [Methylacetylene].** By EDWARD H. KEISER (*Amer. Chem. J.*, 1896, **18**, 328—332; compare Keiser and Breid, Abstr., 1895, 405).—The product of the interaction of alcohols and red-hot magnesium readily evolves a mixture of hydrogen and allylene when placed in water, best containing a little ammonium chloride; the allylene and hydrogen are readily separated by passing the mixture through ammoniacal silver nitrate solution, when silver allylide is precipitated. The maximum yield of the hydrocarbon is obtained with acetone and magnesium; the usual method of preparation is to heat the magnesium in thin-walled iron tubes, closed with an asbestos stopper pierced with holes which serve to admit two glass tubes; through one of these acetone vapour is admitted, whilst gaseous products formed during the action escape through the other. The solid black mass thus produced affords a considerable quantity of allylene when treated in the above manner.

Analyses of the gases, evolved when these products are treated with water, show that they are mixtures of hydrocarbons with free hydrogen; the absence of oxides of carbon leads the author to suppose that a portion of the magnesium combines with the oxygen of the alcohol, the hydrocarbons thus produced combining with a second portion of the magnesium to form magnesium allylide. That the latter substance is present in the black mass appears certain from a consideration of the behaviour of the latter with water, and of the fact that it contains hydrogen; further, when magnesium is burned in oxides of carbon, the residue evolves only minute traces of allylene when treated with water.

The silver and copper precipitates formed on passing the mixed gases into water, appear to be the pure allylides, as, on analysis, they gave numbers agreeing closely with those required for $AgC_3H_3$ and $CuC_3H_3$; the mercury precipitate crystallised from alcohol, and showed the properties of mercury allylide. From determinations of the content of hydrogen in the magnesium residue and of the amount of silver allylide obtained from acetone, it appears that the yield is about one-tenth of that indicated by the equation

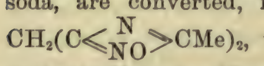
$$2C_3H_6O + 3Mg = 2MgO + Mg(C_3H_3)_2 + 6H.$$

The author is investigating the properties of allylene, and finds that the gas is readily absorbed by sulphuric acid; the product, probably a sulphonic acid, yielding a crystalline barium salt.

A. L.

**Derivatives of Malononitrile.** By HERMANN SCHMIDTMANN (*Ber.*, 1896, **29**, 1168—1175).—Malononitrile, $CH_2(CN)_2$ (1 mol.), when treated with hydroxylamine (1 mol.) yields *cyanethenylamidoxime*, $CN\cdot CH_2\cdot C(NH_2)\colon N\cdot OH$, a rather unstable substance, which melts and decomposes at 124—127°, and yields *acetyl* and *benzoyl derivatives* melting respectively at 142°, and at 184—192° (with decomposition). When treated with double the quantity of hydroxylamine, malononitrile yields *malonediamidoxime*,

$$CH_2[C(NH_2)\colon N\cdot OH]_2,$$

which melts and decomposes at 163—167°; the *diacetyl* and *dibenzoyl derivatives* melt and decompose at 153—159° and 183—185°, and, by prolonged heating at 160° or by boiling with 10 per cent. caustic soda, are converted, respectively into *malonediazoximediethenyl*,  $CH_2(C<^{N}_{NO}>CMe)_2$, which softens at 92° and melts at 99°, and *malonediazoximedibenzenyl*, which melts at 175°.

When malononitrile (1 mol.) is treated with alcoholic sodium ethoxide (1 mol.), a sodium salt, $CHNa(CN)_2$, is formed. If this is treated with 2 mols. of sodium ethoxide, and cyanogen chloride is passed into the solution, *sodiocyanoform*, $CNa(CN)_3$, is formed in amount equal to 70 per cent. of the theoretical; *silver cyanoform* was also prepared and analysed. When the sodium compound is treated with dilute sulphuric acid, nothing separates, but if the whole is now shaken with ether, a separation into three layers ensues, of which the middle layer appears to be cyanoform, the uppermost an ethereal solution of it. *Cyanoform*, $CH(CN)_3$, was obtained as a greenish liquid which, when concentrated in a vacuum beyond a certain point, formed a mass of brownish crystals (polymerisation ?). It crystallises with 1 mol. of methylic or of ethylic alcohol, but the alcohol is not to be regarded simply as alcohol of crystallisation, for these compounds can be crystallised from water without undergoing any change; they soften and turn yellow at 205° and 215° respectively, and finally melt and decompose at 214—215° and 219—220°. It was not found possible, by the action of cyanogen chloride on the sodium derivative, to displace the hydrogen atom in cyanoform by the cyanogen group.

Malononitrile (1 mol.), when dissolved in ice-cold aqueous caustic potash (1 mol.), condenses with diazobenzene nitrate, forming *phenylhydrazonemesoxalonitrile*, $NHPh{\cdot}N{:}C(CN)_2$, a yellow substance which melts and decomposes at 130—144°, dissolves in caustic alkalis but not in alkali carbonates or in acids, and dyes wool yellow.

C. F. B.

**Preparation of Mannose.** By DUYVENÉ DE WITT (*Chem. Centr.*, 1895, ii, 862—863; from *Zeit. Ver. Rübenzuck-Ind.*, 1895, 794—795).—The author recommends the decomposition of the phenylhydrazone of mannose by means of benzaldehyde as a means of obtaining mannose. 1 kilo. of ivory-nut turnings was heated with 2 litres of 6 per cent. hydrochloric acid for six hours, filtered, washed with hot water, the acid solution neutralised with solid sodium carbonate, again filtered, and decolorised with animal charcoal. The requisite quantity of phenylhydrazine hydrochloride and an excess of sodium acetate, dissolved in water, were added, and the crystals thus obtained were heated for two hours with a mixture of benzaldehyde, alcohol, and water, and then filtered. The filtrate, on evaporation in a vacuum, gave a syrup which contained 89·6 per cent. of mannose.

J. J. S.

**Preparation of Glycerose.** By FONZES-DIACON (*Bull. Soc. Chim.*, 1895, [3], **13**, 862—863).—On heating a mixture of anhydrous glycerol and mercuric chloride to 160°, a very energetic action ensues, mercurous chloride being precipitated in large quantity; by prolonging the action, the mercurous chloride itself is completely reduced, and the product obtained on neutralising with sodium carbonate and filtering, is a yellow liquid showing strong reducing properties.

The *osazone* of this compound is readily purified by dissolving it in alcohol and reprecipitating with water. It is a slightly coloured crystalline powder, insoluble in cold water, and melting at 131°, which is the melting point of phenylglycerosazone obtained by Fischer and Tafel (Abstr., 1887, 651) from glycerose. J. F. T.

**Levulose and Humous Substances derived from it.** By BOHUSLAV RAÝMANN and OTTOKAR ŠULC (*Chem. Centr.*, 1895, ii, 593).—Aqueous solutions of pure levulose, when heated to 100—120°, are readily decomposed, an odour of caramel is developed, and humous compounds are formed; the decomposition could not be followed quantitatively by the measure of the rotary or of the reducing power of the solutions. The filtered solution, on distillation with steam, gave a distillate containing furfuraldehyde, formic acid, and formaldehyde, whilst the residue, on evaporation, deposited flocculent humous substances, formed by the decomposition of an acid, $C_6H_8O_5$, which the authors have isolated in the form of its calcium salt, and term *pyrolevulinic acid.* This acid reduces Fehling's solution, and also silver, bismuth, and mercury salts, the metals being deposited. Its reducing power on Fehling's solution is 2·9 times weaker than that of levulose. The analysis of the humous substance indicates the composition $C_{25}H_{22}O_{10}$.

The authors are making experiments to determine whether the decomposition of levulose can be followed quantitatively by estimating the amount of formic acid produced. When treated with dilute sulphuric acid, pyrolevulinic acid is decomposed into carbonic anhydride and an acid probably identical with levulinic acid. J. J. S.

**Nitrogen Pentethyl.** By ARTHUR LACHMAN (*Amer. Chem. J.*, 1896, **18**, 372—375).—In the hope of preparing the compound $N(C_2H_5)_5$, the author studied the action of zinc ethyl on tetrethylammonium iodide. After a mixture of the two substances dissolved in ether had remained for from four to six weeks, it was poured into water whereon an alkaline solution [indicator not given] was obtained which turned yellow, and deposited a finely crystalline, red precipitate, apparently tetrethylammonium tri-iodide. This reaction has not been explained.

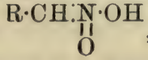
The reaction between zinc ethyl and triethylamine dibromide produces triethylamine, ethylic bromide, and zinc ethobromide; no evidence of nitrogen pentethyl was obtained. Phenylic iodochloride reacts with zinc ethide to form phenylic iodide, ethylic chloride, and zinc chloride and oxychloride. A. G. B.

**The Action of Acid Chlorides on the Salts of the Nitroparaffins.** By JOHN U. NEF and L. W. JONES (*Ber.*, 1896, **29**, 1218—1224).—When benzoic chloride acts on sodium nitroethane, either dissolved in water or suspended in ether, several products are formed. That portion which dissolves in sodium hydrogen carbonate solution consists of *benzoylacethydroxamic acid*, OH·CMe:NOBz, which forms transparent crystals melting at 98—99°. When the ethereal mother liquor from these crystals is treated with light petroleum, transparent crystals, which melt at 69—70°, are formed, but if these are kept, they gradually fall to a white powder which melts at 98°; the compound is identical with benzoylacethydroxamic acid prepared by the action of benzoic chloride on acethydroxamic acid.

The main product of the reaction is, however, neutral, and consists of a mixture of *dibenzoylacethydroxamic acid*, NAcBz·OBz, and *dibenzoylbenzhydroxamic acid*, $NBz_2$·OBz. When the action is carried out in aqueous solution, a small amount of *benzoylethylnitrolic acid*, $NO_2$·CMe:N·OBz, which melts at 133°, is always produced.

When ethylic chloroformate reacts with sodium nitroethane, it appears that derivatives of *carbethoxyacethydroxamic acid*,

OH·CMe:NO·COOEt,

are formed; this crystallises in long needles, and melts at 71—72°. These compounds are accompanied by *carbethoxyethylnitrolic acid*, $NO_2$·CMe:NO·COOEt, which is the main product of the action; it can be prepared by the action of ethylic chloroformate on ethylnitrolic acid, and is a yellowish oil, boiling at 143—144° (pressure = 17 mm.). The author considers that the nitroparaffins have the general formula  $R\cdot CH{:}\underset{\underset{O}{\|}}{N}\cdot OH$, and criticises the views of Hantzsch and Schultze (this vol., i, 353). A. H.

**Action of Nitric acid on Aliphatic Aldehydes.** By Giacomo Ponzio (*J. pr. Chem.*, 1896, [2], **53**, 431—432).—From analogy with the action of nitric acid on ketones (Fileti and Ponzio, Abstr., 1895, i, 499), the author expected that by substituting aldehydes for ketones, oximidoaldehydes would be formed, which would break up into keto-aldehydes and dinitrohydrocarbons; this seems to be the course of the change, although the final products are fatty acids, hydroxylamine, and dinitrohydrocarbons. Thus, œnanthaldehyde yielded dinitrohexane, hydroxylamine, and heptoic acid.

A. G. B.

**Action of Alcoholic Potash on Isovaleraldehyde.** By Leopold Kohn (*Monatsh.*, 1896, **17**, 126—148).—The author has previously shown (this vol., i, 10) that no secondary glycol is formed by the action of alcoholic potash on valeraldehyde, the chief products being two oily substances which are best separated by fractional distillation under diminished pressure. A small quantity of isovaleric acid is formed at the same time. One of these oils, which distils at 86° (20 mm. pressure), or at 187—191° (746 mm. pressure), is a mobile liquid, and has a strong odour; it is an unsaturated aldehyde, $C_{10}H_{18}O$, but as it is very readily oxidised by atmospheric oxygen, it is almost impossible to obtain it free from the corresponding acid, $C_{10}H_{18}O_2$. This aldehyde is beyond doubt identical with the substance described by Barbier and Bouveault (Abstr., 1895, i, 644), and also by Gäss. It yields an *oxime*, $C_{10}H_{18}{:}N\cdot OH$, which is a colourless liquid boiling at 125° (20 mm. pressure), and this, when treated with acetic anhydride, yields the *nitrile*, $C_{10}H_{17}N$, a colourless, mobile oil, with a penetrating odour. The nitrile, when hydrolysed with alcoholic potash at 180°, is converted into the acid $C_{10}H_{18}O_2$.

The *phenylhydrazone*, $C_{10}H_{18}{:}N\cdot NHPh$, crystallises in colourless plates which melt at 133°. The unsaturated nature of the aldehyde is shown by the fact that it readily unites with bromine to form a dibromide, $C_{10}H_{18}Br_2O$.

When the aldehyde is oxidised by atmospheric oxygen, by chromic acid mixture, or by potassium permanganate, it yields the *acid* $C_{10}H_{18}O_2$. This is a colourless, oily liquid boiling at 140° under a pressure of 19 mm., its *calcium* salt is sparingly soluble in water, its *silver* salt, $C_{10}H_{17}O_2Ag$, is soluble in hot alcohol, and its *dibromide* crystallises from benzene in brilliant, glistening prisms, which melt at 135°, and are identical with Hell and Schoop's dibromocapric acid (Abstr., 1879, 715).

The unsaturated acid, $C_{10}H_{18}O_2$, when oxidised according to Fittig's method with a 2 per cent. permanganate solution, yields a dihydroxycapric acid, which must be the αβ-dihydroxy acid, since it yields no lactone; it follows, therefore, that the acid $C_{10}H_{18}O_2$ is an $\alpha\beta$-unsaturated acid, *α-isopropyl-β-isobutylacrylic acid*,

$$CHMe_2\cdot CH_2\cdot CH\colon C(COOH)\cdot CHMe_2.$$

This view is supported by the fact that the aldehyde $C_{10}H_{18}O$, when oxidised with potassium permanganate, yields, besides the acid previously mentioned, small quantities of isobutyric and isovaleric acids.

The second compound obtained by the action of alcoholic potash on valeraldehyde is a colourless, oily liquid with only a faint odour; it boils at 140—146° under a pressure of 18 mm., and has the composition $C_{10}H_{20}O_2$. It yields an oily hydrazone, but no oxime and no acetyl derivative. J. J. S.

**Syntheses by means of Zinc Chloride.** By Iwan L. Kondakoff (*J. Russ. Chem. Soc.*, 1894, **26**, 5—20; compare Abstr., 1893, i, 382; 1894, i, 113).—The reactions taking place between ethylene hydrocarbons, like trimethylethylene, isobutylene, symmetrical methylethylethylene, or propylene, and acid chlorides, like acetic chloride, in the presence of a small quantity of zinc chloride are characterised by great development of heat.

With trimethylethylene, two products are obtained, one a ketone, $CMe_2Cl\cdot CHMe\cdot COMe$, is a colourless liquid, boiling at 75—78° under 31 mm. pressure, which, with phenylhydrazine, gives a crystalline *phenylhydrazone*, showing all the reactions of the pyrazolones. The chloroketone is broken up by alkalis into hydrogen chloride and the ketone $CMe_2\colon CMe\cdot COMe$, a homologue of mesityl oxide, boiling at about 147°. This energetically combines with bromine forming colourless, tabular crystals, melting at 93°. The oxime boils at 106—110° under 31 mm. pressure. Sodium hydrogen sulphite forms a crystalline compound with the ketone. When the ketone is distilled with dilute acids, it breaks up, similarly to mesityl oxide, into acetone and methyl ethyl ketone.

Isobutylene gives only mesityl oxide, boiling at 129—130°.

*Symmetrical methylethylethylene* yields secondary amylic chloride, boiling at 104—106°; a saturated *ketone*, boiling at 195—200°; and an unsaturated *ketone*, boiling at 153—159°. The latter is decomposed by acids into propaldehyde and methyl ethyl ketone, and has the structure, $CH_2Me\cdot CH\colon CMe\cdot COMe$.

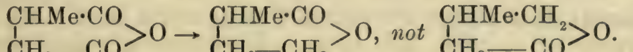
Propylene gives two products, one boiling at 38° (isopropylic chloride), the other at 80°, under 20 mm. pressure; the latter unites with bromine, but does not react with silver oxide or hydroxylamine. A β-chloroketone, $CHMeCl\cdot CH_2\cdot COMe$, is first formed, which, losing the elements of hydrogen chloride, gives the ketone $CHMe\colon CH\cdot COMe$, isopropylic chloride being simultaneously formed. S. G. R.

**Products of the Distillation of Wood.** By Ernest Barillot (*Compt. rend.*, 1896, **122**, 735—736).—Experiments on an industrial scale confirm the results obtained in the laboratory (this vol., i, 403), but the yield of calcium acetate does not vary in the same way as the yield of acetic acid in the laboratory experiments, a result probably dependent on the real nature of the acids which are regarded as "acetic acid." C. H. B.

**Distillation of Acids of the Acetic Series.** By E. Sorel (*Compt. rend.*, 1896, **122**, 946—948).—The author has applied to mixtures of water and each of the first four acids of the acetic series the method of fractional distillation previously applied to aqueous alcohol (Abstr., 1893, ii, 347), the composition of the vapour at each instant being calculated from the curve representing the variations in the composition of the liquid in the retort. A table is given showing the results for proportions of acid varying from 1 per cent. to 70 per cent.

In dilute solutions, the proportion of acid in the vapour is higher the higher the molecular weight of the acid, but when the concentration increases, the reverse is the case, and the proportion is lower the higher the molecular weight of the acid. As a result, mixtures of propionic or butyric acid and water of a certain composition distil unchanged, as if they were definite hydrates. Butyric acid, moreover, shows a peculiar phenomenon, and with any proportion of acid between 24 to 34 per cent. the composition of the distillate is independent of the composition of the liquid in the retort. Its behaviour is intermediate between that of miscible liquids and liquids which are partially or completely insoluble in one another.
C. H. B.

**New Method of preparing Aliphatic Lactones.** By Fritz Fichter and A. Herbrand (*Ber.*, 1896, **29**, 1192—1195).—Lactones may be obtained by reducing the anhydrides of appropriate dibasic acids; pyrotartaric anhydride yields $\alpha$- (not $\beta$-) methylbutyrolactone.



$$\left.\begin{array}{l}\mathrm{CHMe{\cdot}CO}\\ |\\ \mathrm{CH_2{-}{-}CO}\end{array}\right>\mathrm{O} \rightarrow \left.\begin{array}{l}\mathrm{CHMe{\cdot}CO}\\ |\\ \mathrm{CH_2{-}CH_2}\end{array}\right>\mathrm{O},\ \textit{not}\ \left.\begin{array}{l}\mathrm{CHMe{\cdot}CH_2}\\ |\\ \mathrm{CH_2{-}{-}CO}\end{array}\right>\mathrm{O}.$$

The anhydride is dissolved in plenty of ether, the solution poured on to some lumps of 4—5 per cent. sodium amalgam in a conical flask, and a slight excess of dilute hydrochloric acid (1 : 1) run in under the ethereal solution, acid and amalgam being used in twice the theoretical amount. The yield was 10—20 per cent. of the theoretical.

In this way, succinic anhydride yields butyrolactone, and pyrotartaric anhydride yields the lactone prepared by Hjelt (Abstr., 1884, 297); this is shown to be $\alpha$-methylbutyrolactone (not $\beta$), because it yields methylethylacetic acid when reduced with hydriodic acid and phosphorus. Glutaric anhydride appears to yield not a lactone, but $\delta$-hydroxyvaleric acid. C. F. B.

**Action of Ethylic Orthoformate on Ethereal Salts of Ketonic acids, on Ketones, and on Aldehydes.** By Ludwig Claisen (*Ber.*, 1896, **29**, 1005—1008).—Ethylic orthoformate condenses with ethylic acetoacetate under certain conditions to form *ethylic ethoxymethyleneacetoacetate*, $\mathrm{OEt{\cdot}CH{:}CAc{\cdot}COOEt}$, under others to form ethylic ethoxycrotonate, $\mathrm{OEt{\cdot}CMe{:}CH{\cdot}COOEt}$. From the latter, the *acid* can be prepared; it readily loses carbonic anhydride, forming *isacetone ethyl ether*, OEt·CMe:CH$_2$, which boils at 62°. In the same way ethylic benzoylacetate, yields *ethylic β-ethoxycinnamate*,

OEt·CPh:CH·COOEt,

boiling at 171—173° under 17 mm. pressure; *β-ethoxycinnamic acid*, OEt·CPh:CH·COOH, melting at 162°, with evolution of carbonic anhydride; and *ethoxystyrene*, OEt·CPh:CH$_2$, which boils at 209—210°, and has a sp. gr. = 0·973 at 15°. *Ethylic acetonedicarboxylate* yields *ethylic ethoxyglutaconate*, COOEt·CH:C(OEt)·CH$_2$·COOEt, boiling at 146—147° under 11 mm. pressure; the *acid* melts at 182—183° with evolution of carbonic anhydride.

In reality, the first action of ethylic orthoformate on the acetoacetate is to replace the two methylene hydrogen atoms by ethoxyl groups, and by working at a low temperature a large yield of *ethylic β-diethoxybutyrate*, CMe(OEt)$_2$·CH$_2$·COOEt, can be obtained. This, when distilled, splits up into alcohol and the ethoxycrotonate, and it, or rather its sodium derivative, can be formed from the ethoxycrotonate by dissolving this in alcoholic sodium ethoxide. *Sodium diethoxybutyrate* crystallises well; the free *acid* is unstable, and, when distilled, decomposes into carbonic anhydride and the compound CMe$_2$(OEt)$_2$, analogous to acetal, and boiling at 114°. The last compound can be obtained more easily by the action of ethylic orthoformate on acetone. From benzophenone, however, no analogous derivative could be so prepared.

In a similar manner ethylic orthoformate acts on aldehydes, converting them into acetals, CHR(OEt)$_2$. Those from benzaldehyde and from furfuraldehyde were prepared; the latter boils at 187—190°.

C. F. B.

**Specific Refractive Power of Pyrotartaric acid.** By ALBERT LADENBURG (*Ber.*, 1896, **29**, 1254).—The following values have been obtained at 22° in aqueous solution. Per cent. of acid, 18·66, 19·58, 29·27; angle of refraction, 1·95°, 2°, and 3·112°; sp. gr., 1·0445, 1·045, and 1·074; $[\alpha]_D$ = 10·01°, 9·774°, and 9·9° respectively; the mean for $[\alpha]_D$ = 9·89°. The concentration of the solution has very little influence on the refractive power. These values are to be substituted for those previously given (Abstr., 1895, i, 449). J. B. T.

**Replacement of Carboxyl by Amidogen in Polybasic acids.** By THEODOR CURTIUS and HANS CLEMM (*Ber.*, 1896, **29**, 1166—1167).—The following substances have been prepared from *suberic acid*, by the reactions indicated in Abstr., 1894, i, 331. The *hydrazide*,

$C_6H_{12}(CO·NH·NH_2)_2$,

and *azoimide*, $C_6H_{12}(CO·N_3)_2$, melting respectively at 185—186° and 25°. *Hexamethylenediethylurethane*, $C_6H_{12}(NH·COOEt)_2$, melting at 84°. *Hexamethylenediamine*, $C_6H_{12}(NH_2)_2$, melts at 40° and boils at 192—195°; its *hydrochloride* remains unmelted at 270°, its *dibenzoyl derivative* melts at 154—155°. C. F. B.

**Action of Light on Organic acids in presence of Uranium Salts.** By HENRY FAY (*Amer. Chem. J.*, 1896, **18**, 269—290).—The equation given by Seekamp (*Annalen*, 1862, **122**, 115) as representing the action of uranyl oxalate on oxalic acid is incorrect, as it does not account for the production of formic acid or of carbon monoxide. An unpublished investigation by Harry C. Jones has shown that the acid is decomposed with production of one molecular proportion of carbonic anhydride, the nature of the precipitate subsequently formed being dependent on the relative amounts present of uranyl oxalate and free oxalic acid, but is almost always a mixture of amorphous and crystalline substances. The green crystals proved to be hydrated uranous oxalate, $U(C_2O_4)_2 + 6H_2O$, and are obtained in a pure state when a large excess of oxalic acid is present. Further, a very small quantity of uranyl oxalate suffices for the decomposition of a very large, possibly unlimited, quantity of free oxalic acid, provided the action is a continuous one. It is probable that the uranyl salt acts in some way as an oxidising agent.

In continuation of the above work, the author has carried out experiments with the following results. The brown, amorphous precipitate is also produced when a solution of uranyl oxalate is exposed to sunlight, but is not then accompanied by gaseous products; it contains 77·15—78·47 per cent. of ammonia, and cannot be a hydrated oxide, as was at first supposed, since it contains carbon. When heated alone, it evolves a small quantity of carbonic oxide, but, owing to the small percentage of carbon in the substance, its relative amount could not be ascertained. If allowed to remain in a desiccator during a few days, it changes to a yellow *substance* containing 8·04—8·7 per cent. of water, 74·9—75·46 per cent. of uranium, and 1·02—1·36 per cent. of carbon. As all attempts to cause the union of carbonic oxide and water in presence of ammonium salts have given negative results, it follows that the formic acid produced in the above decomposition is formed directly from the oxalic acid. The isolation of acids from the above compounds was attempted, but without success.

Solutions of potassium uranyl malonate, with or without free malonic acid, when exposed to sunlight during several days, showed no signs of decomposition. Seekamp's observation (*loc. cit.*) that succinic acid is decomposed in presence of uranium nitrate into carbonic anhydride and propionic acid was verified, but the green precipitate simultaneously formed gave, on analysis, numbers not in agreement with those required for uranous succinate. A solution of tartaric acid and uranyl nitrate gradually assumes a deep green colour when exposed to sunlight, a light green salt of uncertain character being subsequently deposited; the production of the latter is greatly promoted by heat, but in no case has gas been evolved. Acetic, propionic, and isobutyric acids, when exposed to direct sunlight in presence of uranium salts, are decomposed into the corresponding hydrocarbons and carbonic anhydride. A. L.

**A peculiar class of Platinic Compounds and the Isomeric Platoso-oxalic acids.** By ALFRED WERNER (*Zeit. anorg. Chem.*, 1896, **12**, 46—54).—The author has examined a series of salts of the formula $PtPyCl_3R$ and $PtPyCl_5R$ (where Py = pyridine, R = K, Li, or

Na), which are analogous to the salts $Pt(CN)_4Cl_2K_2$ and $Pt_4(CN)_4Br_2K_2$ examined by Hadow (this journal, 1860, **13**, 106). When chlorine is passed into a concentrated solution of the salt, $PtPyCl_3K$, a magma of beautiful, copper-coloured leaflets is at first obtained, and on further treatment with chlorine a precipitate of silky, bright yellow needles of the salt $PtPyCl_5K$ is formed. When a small quantity of the salt $PyPtCl_5K$ is added to a solution of the salt $PyPtCl_3K$, the above copper-coloured compound is at once formed. By the action of bromine on the salt $PyPtCl_3K$, analogous compounds containing bromine are obtained.

The salt $NH_3PtCl_3K$ behaves in a similar manner; when a small quantity of the salt $NH_3PtCl_5K$ is added at a certain temperature of the solution, a compound crystallising in lustrous, green leaflets is deposited, but is converted into the salt $NH_3PtCl_3K,H_2O$ as the mixture cools.

When platinisodium oxide is treated with oxalic acid at temperatures below 100°, the copper-coloured salt described by Doebereiner (*Ann. Phys. Chem.*, 1832, **27**, 243), together with a small quantity of a bright yellow salt, is formed; the latter can also be obtained from the former by heating the solution with a small quantity of sodium hydroxide. The yellow salt is reconverted into the copper-coloured salt by treatment with chlorine. A salt crystallising in yellowish-red needles is obtained by boiling platinisodium oxide with oxalic acid, and when this salt is mixed with the yellow salt the copper-coloured salt is obtained. From these results, the author concludes that the copper-coloured modification of sodium platoso-oxalate is not isomeric with the yellow modifications, but that these are additive compounds of platoso-oxalates and platinoxalates. E. C. R.

**Formation of Carbon Chains: III. Reaction of Ethylic Chloracetate with Ethylic Sodiomalonate and Sodacetoacetate.** By CARL A. BISCHOFF (*Ber.*, 1896, **29**, 966—971).—It is known that when an attempt is made to prepare the derivative $CHR(COOEt)_2$ by the action of RX [X = Cl, Br, or I] on ethylic sodiomalonate, $CHNa(COOEt)_2$, a certain amount of the compound $CR_2(COOEt)_2$ and $CH_2(COOEt)_2$ is formed at the same time, if the radicle R has a "negative" character; for example, $CH_2Ph$ or $CPh_3$. This may be ascribed to a migration of the sodium atom to the compound $CHR(COOEt)_2$, when this has been formed, under the attracting influence of the negative group R. If this explanation be correct, it should be possible, by the action of ethylic chloracetate, on the sodiomalonate, to get not only the normal condensation product $COOEt{\cdot}CH_2{\cdot}CH(COOEt)_2$, but also some of the compound $(COOEt{\cdot}CH_2)_2C(COOEt)_2$. This, as a matter of fact, is the case; but yet the explanation given is not sufficient, for ethylic bromopropionate yields only the normal product; stereochemical relations are obviously concerned. Ethylic sodacetoacetate behaves in much the same way as the sodiomalonate.

*Methylic pentandioic-3-dimethyloate* $(COOMe{\cdot}CH_2)_2C(COOMe)_2$, which appears not to have been described before, boils at 187°.

C. F. B.

**Formation of Carbon Chains: IV, V, VI. Reaction of Ethylic Sodioalkylmalonates and Sodioalkylacetoacetates with the Ethylic Salts of α-Bromo-fatty acids.** By CARL A. BISCHOFF (*Ber.*, 1896, **29**, 972—978, 979—982, 982—989; compare this vol., i, 84).—In order to study the comparative ease with which different radicles can be introduced into an already existing complex, the reaction which the sodium derivatives of ethylic malonate and of its methyl, ethyl, propyl, isopropyl, isobutyl, isoamyl, and allyl derivatives undergo with the α-bromo-derivatives of ethylic propionate, butyrate, isobutyrate, and isovalerate, has been examined in detail. In each case, 70 c.c. of absolute alcohol containing 4·6 grams of sodium (1 atom) in solution was mixed with the malonate (1 mol.) and the ethylic bromo-salt (1 mol.), and the mixture heated on the water bath until it became neutral to phenolphthaleïn, the eight malonic derivatives being heated separately with one of the bromo-salts in the same bath at the same time. The time that elapsed before the mixture became neutral varied greatly, but it never exceeded two hours in the case of the bromopropionate and bromobutyrate, or four in the case of the bromisobutyrate, and was eight hours, on the average, in the case of the bromisovalerate. When the action was ended, the mixture was diluted with 50 c.c. of ether, and filtered from the salt that separated; the latter being washed with two successive quantities of 10 c.c. of ether. The combined filtrates were then heated at 100—105° until no more ether distilled over, and the residue twice distilled under atmospheric pressure, fractions being collected at intervals of 10° in the first distillation, of 5° in the final one. A curve was then constructed in which the weights of the final fractions were plotted as ordinates and the temperatures at which they boiled as abscissæ; a number of such curves is reproduced in the paper. As a rule, each curve exhibits two maxima; one near the boiling points of the two ethereal salts which were taken, the other near that of their normal condensation product. The higher the second maximum relatively to the first, the greater is the amount of condensation that has taken place. In no case was the formation of a *di*-substitution product of the malonate indicated by the curve (compare preceding abstract).

Similar experiments were made, using, instead of ethylic malonate and its above-named derivatives, ethylic acetoacetate and its corresponding derivatives.

The following conclusions are drawn from the results of the experiments. (I) All the malonic derivatives yield condensation products more readily than the corresponding acetoacetic derivatives. (II) As regards their power of condensing with malonic and acetoacetic derivatives, the ethylic bromo-salts arrange themselves in the following order of decreasing condensibility: propionic, butyric, isobutyric, isovaleric. Ethylic α-bromisobutyrate will hardly condense with acetoacetates; it condenses in the β-position with mono-substituted malonates. (III) The malonic derivatives arrange themselves in the following order of decreasing condensibility: ethylic malonate, and then the methyl, ethyl, propyl, allyl, isoamyl, isobutyl, and isopropyl derivatives; the last hardly reacts at all. (IV) With the acetoacetic derivatives, which react much less readily, the limit of condensibility is already reached at the ethyl derivative, which hardly yields any condensation product. C. F. B.

**Formation of Carbon Chains. VII. Conjugated Ethereal Malonates with Single Linking.** By CARL A. BISCHOFF (*Ber.*, 1896, **29**, 1276—1280).—Diethylic malonate and diethylic bromomalonate in presence of sodium ethoxide yield chiefly tetrethylic ethanetetracarboxylate with some tetrethylic ethylenetetracarboxylate. It is doubtful whether the hexabasic acid,

$$CH(COOR)_2{\cdot}C(COOR)_2{\cdot}CH(COOR)_2,$$

is formed even in traces; the ethylenetetracarboxylate was probably derived from a little dibromomalonate in the monobromo-compound. Under similar conditions, dimethylic malonate, methylic bromomalonate, and sodium methoxide yield dimethylic malonate, methylic ethanetetracarboxylate, and the *methylic* salt of the above hexabasic acid (*propanehexacarboxylic acid pentanedioictetramethyloic* 2 : 3 : 3 : 4-*acid*). It is separated by distillation under reduced pressure, boils at 250—255° (26 mm.), melts at 136°, is sparingly soluble, and, when hydrolysed by means of hydrochloric acid, yields tricarballylic acid. These results are in complete accordance with the "dynamic" hypothesis. Methylic ethanetetracarboxylate may be readily prepared from sodium methoxide, methylic malonate, and iodine in molecular proportion; the first two are mixed, and the crystalline mass thoroughly incorporated with solid iodine, the temperature being maintained below 20°. The ethylic salt acts in a similar manner; in neither case is any hexabasic acid formed. The methylic salt, $OH{\cdot}C[CH(COOMe)_2]_3$, obtained by Zelinsky and Porchunow (this vol., i, 135) from diethylic sodiomalonate and carbon tetrachloride, is probably identical with the above salt of the hexabasic acid.

J. B. T.

**Formation of Carbon Chains. VIII. Conjugated Dimethylic Malonates with Double Linking.** By CARL A. BISCHOFF (*Ber.*, 1896, **29**, 1280—1286).—Sodium methoxide and dimethylic bromomalonate readily react; the chief product is the propanehexacarboxylic acid, $(COOR)_2CH{\cdot}C(COOR)_2{\cdot}CH(COOR)_2$ (compare preceding abstract), which was identified by the production of tricarballylic acid when hydrolysed, but ethylenetetracarboxylic acid, is also formed. As a portion of the crude product (b. p. 150—220°, 10 mm.) when hydrolysed gives maleïc acid and, in traces, fumaric acid, tetramethylic mesoxylate (b. p. 215—220°) is apparently also formed. Probably a bromo-acid, $CH(COOR)_2{\cdot}C(COOR)_2{\cdot}CBr(COOR)_2$, is first produced, the group $R_3CBr$ being then converted into $R_3CH$, thus: $R_3CBr + (COOMe)_2CHBr + 2NaOMe = 2NaBr + R_3CH + (COOMe)_2C(OMe)_2$. Ethylenetetracarboxylic acid is formed by treating tetramethylic ethanetetracarboxylate with bromine at 190° or with iodine and sodium methoxide at low temperatures. The *methylic* salt crystallises in long, thick needles or prisms, melts at 121°, and yields maleïc anhydride and fumaric acid when hydrolysed. The hexabasic acid (*loc. cit.*) is also formed in considerable quantity. Dimethylic chloromalonate differs from the bromo-derivative in its behaviour towards sodium methoxide; the reaction proceeds more slowly, and hydrolysis occurs to a large extent. The fraction boiling at 215—220° under the ordinary pressure probably contains tetramethylic mesoxalate, which is frequently produced by the decomposition of chloromalonates. The portion boiling at about 180° (20 mm.) melts at 105—120°, and, when hydrolysed by means of hydrochloric acid, yields fumaric acid and, in larger quantity, succinic acid, proving that the original fraction must have contained tetramethylic ethylenetetracarboxylate and tetramethylic ethanetetracarboxylate respectively. J. B. T.

**Formation of Carbon Chains. IX. Conjugated Diethylic Malonates with Double Linking.** By CARL A. BISCHOFF (*Ber.*, 1896, **29**, 1286—1293).—The author's object was to ascertain whether in the ethylic series, in addition to or instead of the normal product, $C(COOEt)_2:C(COOEt)_2$, the hexabasic compound

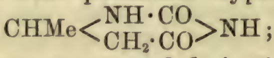
$$CH(COOEt)_2\cdot C(COOEt)_2\cdot CH(COOEt)_2$$

is also formed, or whether the production of this is dependent on the presence of the methoxy-group; also whether differences exist between ethylic bromo- and chloro-malonate similar to those between the corresponding methylic salts. The "dynamic hypothesis" indicates that whilst the bromine favours the reaction, this tendency might be neutralised by the ethylic group.

The interaction of sodium ethoxide and diethylic chloromalonate has been studied by Conrad and Guthzeit, who obtained ethylic ethylenetetracarboxylate together with considerable quantities of oil, amounting in some cases to 60 per cent.; ethylic ethanetetracarboxylate was isolated in small quantity from this, but no tricarballylic acid could be obtained by the hydrolysis of the highest fraction. Diethylic chloromalonate therefore behaves like the methylic salt (compare preceding abstract).

Diethylic bromomalonate and sodium ethoxide yield only tetraethylic ethylenetetracarboxylate; this, by the action of phenylhydrazine, gives the phenylhydrazide described by Ruhemann (Abstr., 1894, i, 14), together with ethylic ethanetetracarboxylate, which, by the further action of phenylhydrazine, gives the same phenylhydrazide. Dipotassium dihydrogen ethylenetetracarboxylate, obtained by the hydrolysis of the tetrethylic salt when suspended in benzene and treated with dry chlorine, yields the *acid*; this crystallises from ether in small, colourless, quadratic plates, and from water in short, quadratic prisms containing $1\frac{1}{2}$ $H_2O$. The tetrapotassium salt crystallises with $2H_2O$ in hexagonal plates which quietly char when heated. The *zinc* salt crystallises with $4\frac{1}{2}$ $H_2O$; when dried and then exposed to air, a salt containing $1H_2O$ is formed. These normal salts are all stable when heated, but the dipotassium salt at 150° evolves carbonic anhydride and then water; the acid when heated at 163—164° evolves gas; when slowly heated, fumaric acid is formed, but if quickly heated or distilled, dimethylmaleïc anhydride (pyrocinchonic acid) is produced. The fact that ethylenetetracarboxylic acid should exhibit no tendency to form an anhydride, whilst its hypothetical decomposition product, dimethymaleïc acid, yields one so readily, is of considerable interest. J. B. T.

**Decomposition of Acid Amides.** By Hugo Weidel and E. Roithner (*Monatsh.*, 1896, **17**, 172—190; compare A. W. Hofmann, Abstr., 1882, 822, 950, 1052; 1883, 789; 1884, 1114; Hoogewerff and van Dorp, Abstr., 1886, 1194; 1889, 981; 1891, 196 and 1216).—Succinamide when treated with potash and bromine in quantities required by the equation $C_4H_8N_2O_2 + 2KOH + 4Br_2 = C_4H_6N_2O_2 + 2KBr + 2H_2O$, yields a substance isomeric with α-lactylcarbamide (Urech, *Annalen*, **165**, 99), which the author terms *β-lactylcarbamide.* The yield, if too much hypobromite is not used and if the temperature is kept low, amounts to 55—60 per cent. It crystallises in brilliant, glistening, prismatic needles, melts at 275° (uncorr.), and is very sparingly soluble in cold water or alcohol, but readily in hot; ether and benzene even when hot dissolve only minute quantities. In chemical properties, the substance behaves like a weak monobasic acid; the *sodium* and *potassium* derivatives are extremely deliquescent; the *silver* compound, $C_4H_5AgN_2O_2$, is a colourless precipitate, consisting of minute crystals, and is almost insoluble in hot water. When heated with acetic anhydride, it yields a *monacetyl* derivative, which crystallises in colourless, glistening, monoclinic needles, melts at 180° (uncorr.), and is readily soluble in warm alcohol or ethylic acetate.

If β-lactylcarbamide is heated with concentrated hydrochloric acid in sealed tubes at 160°, it is decomposed into β-amidopropionic acid, carbonic anhydride, and ammonia; when treated with alcohol, β-amidopropionic acid hydrochloride is converted into *ethylic β-amidopropionate hydrochloride*, which is readily soluble in alcohol and water, but insoluble in ether; it melts at 69—71° (uncorr.), and the yield is almost theoretical. Concentrated aqueous soda decomposes β-lactylcarbamide in a similar manner. The author has succeeded in synthesising β-lactylcarbamide by heating equivalent quantities of carbamide and β-amidopropionic acid, first at 180°, and then at 210—220°. The amide of pyrotartaric acid, prepared by Henry's method (Abstr., 1886, 886), melts at 225°, and not at 175° (Henry), and when treated with potassium hypobromite, yields *β-methyl-β-lactylcarbamide*,  $CHMe<\begin{matrix}NH\cdot CO\\CH_2\cdot CO\end{matrix}>NH$; this is a colourless syrup, and also yields a syrupy *acetyl* derivative. When heated with concentrated hydrochloric acid at 160°, it is decomposed into β-amidobutyric acid, carbonic anhydride, and ammonia.

*β-Amidobutyric acid* crystallises in colourless needles, melts at 184° (uncorr.), is insoluble in absolute alcohol and in ether, and yields a well-defined *platinochloride*, $(C_4H_9NO_2)_2,H_2PtCl_6$. When treated with nitrous acid, it is converted into a syrupy hydroxybutyric acid, and this, if acted on with phosphorus pentachloride and then with alcohol, yields Balbiano's ethylic β-chlorobutyrate.

Malonamide is completely destroyed when treated with potassium hypobromite, but when malonamide (1 mol.) is treated first with bromine (1 mol.), and then, after some time, with dilute potash (1/5 normal), until neutral, and when the crystalline compound thus obtained is warmed with potash, hydantoïc acid is formed; the yield is, however, very poor. J. J. S.

**Action of Carbamide and Thiocarbanilide on Acid Anhydrides.** By FREDERICK L. DUNLAP (*Amer. Chem. J.*, 1896, **18**, 332—341).—Phthalimide is the sole product of the interaction of phthalic anhydride and carbamide at 150° (compare Piutti, Abstr., 1882, 1297) and is thus readily obtained in a pure condition. *Dichloromaleïnuric acid*, $COOH\cdot CCl\colon CCl\cdot CO\cdot NH\cdot CO\cdot NH_2$, is produced when a mixture of dichloromaleïc anhydride and carbamide in molecular proportions is heated at 90—95° for 20 minutes; it crystallises from alcohol in transparent prisms with truncated ends, and melts and decomposes at 158°. It is very sparingly soluble in all ordinary solvents with the exception of hot water. The product of its decomposition at 158° is dichloromaleïmide, which is also formed directly when the mixture of dichloromaleïc anhydride and carbamide is heated at 110—115° for 15 minutes. Carbamide and dichloromaleïc anhydride, when heated together at 100—105°, yield *dibromomaleïnuric acid*, $COOH\cdot CBr\colon CBr\cdot CO\cdot NH\cdot CO\cdot NH_2$; this is insoluble in light petroleum, benzene, carbon bisulphide, and water, but dissolves in alcohol, chloroform, and ether, and is readily soluble in acetone; it separates from alcohol in tufts of prisms with doubly truncated terminations; it melts and decomposes at 191°, yielding dibromomaleïmide, which may be conveniently obtained by heating a mixture of dibromomaleïc anhydride and carbamide at 135°. Succinimide is readily obtained by distilling a mixture of succinic anhydride and carbamide; the intermediate product, succinuric acid, melts at 211—211·5°, and not at 203—205° as stated by Pike (this Journal, 1874, **27**, 49).

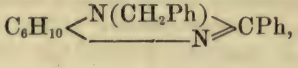
Thiocarbanilide and phthalic anhydride interact at 125—130°, the products being phthalanilic acid, and phenylthiocarbimide; diphenylthiophthaluric acid, probably the intermediate substance, could not be isolated. At 170—175° the products are phthalanil, thiocarbonic anhydride, and aniline. Phthalanilic acid is insoluble in benzene, chloroform, light petroleum, and ether, very sparingly soluble in acetone, but is slightly soluble in boiling water; Laurent and Gehrhardt gave its melting point as 192°, Zincke and Cooksey (Abstr., 1890, 784) as 158°, and J. F. Thorpe (Abstr., 1893, i, 466) as 191—193°. The authors now find that the substance, prepared by several methods, always melts at 169—169·5°, simultaneously evolving gases and forming phthalanil, which melts at 204°.

Thiocarbanilide and succinic anhydride at 130—150° give thiocarbonic anhydride, succinanil and aniline, together with a substance sparingly soluble in hot alcohol and melting at 226°; a small quantity of phenylthiocarbimide is formed at 130—135°. A. L.

**Condensation of Aldehydes with Ethylic Acetonedicarboxylate.** By PAVEL I. PETRENKO-KRITSCHENKO and S. STANIS-

CHEWSKY (*Ber.*, 1896, **29**, 994—996).—*Ethylic dimethyltetrahydropyronedicarboxylate*, $CO<\begin{matrix}CH(COOEt)\cdot CHMe\\CH(COOEt)\cdot CHMe\end{matrix}>O$, is formed when gaseous hydrogen chloride is led into a mixture of ethylic acetonedicarboxylate (1 mol.) and acetaldehyde (2 mols.). It melts at 102°, and boils at 195—200° under 68 mm. pressure; it gives a red coloration with alcoholic ferric chloride; it is not acted on by boiling acetic chloride or phosphorus trichloride, but the pentachloride reacts with it at 100°. The corresponding *diphenyl* compound was prepared in a similar manner, using benzaldehyde; it melts at 115°, and reacts like the dimethyl compound; a bye-product, melting at 148°, was also obtained. C. F. B.

**Orthohexamethylenediamine.** By ALFRED EINHORN and BENJAMIN S. BULL (*Ber.*, 1896, **29**, 964—965).—Ethylic hexahydroanthranilate (Abstr., 1894, i, 591) yields the *amide* when treated with alcoholic ammonia. This melts at 153·5°, and, when its hydrobromide is oxidised with hypobromite, loses 2 atoms of hydrogen, yielding the compound $C_7H_{12}N_2O$; this melts at 230—232°, reduces Fehling's solution, and yields a nitroso-derivative. Its constitution is as yet undetermined; it is stable towards alkalis, but treatment with hydrochloric acid readily converts it into *orthohexamethylenediamine*, $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot NH_2\\ | \qquad\qquad | \\CH_2\cdot CH_2\cdot CH\cdot NH_2\end{matrix}$, of which the *dihydrochloride* was prepared, and also the condensation product with benzaldehyde, namely, hexahydro-orthophenylenebenzylamidine,



$$C_6H_{10}<\begin{matrix}N(CH_2Ph)\\ \underline{\qquad\qquad} N\end{matrix}\gg CPh,$$

melting at 132·5°. C. F. B.

**Sandmeyer's Reaction.** By JOHANN WALTER (*J. pr. Chem.*, 1896, [2], **53**, 427—430).—Votoček has stated (*Chem. Zeit. Rep.*, 1896, **20**, 70), that the quantity of cuprous chloride may be reduced to 1/21 and 1/28 mol. per mol. of amine without appreciably influencing the yield of chlorobenzene and metachloronitrobenzene respectively in the well-known reaction. The author holds the view that the mechanism of the change consists in the reduction of diazobenzene chloride to phenylhydrazine by the cuprous chloride which thus becomes cupric chloride; the phenylhydrazine is then oxidised in the presence of hydrochloric acid to chlorobenzene by the cupric chloride; the cuprous chloride would thus be again formed to take its part in the cycle of changes once more. It was found that phenylhydrazine in presence of hydrochloric acid is oxidised to chlorobenzene by both cupric chloride and ferric chloride; and although it was found impossible to detect phenylhydrazine as an intermediate product in the Sandmeyer reaction, this may be because it is oxidised as soon as formed. In the fact that a copper salt is not essential to the production of iodobenzene by this method, the author sees a confirmation of his view, since hydriodic acid is itself a reducing agent.

A. G. B.

**Isomerism in the Benzene Series.** By William Oechsner de Coninck (*Compt. rend.*, 1896, **122**, 736—737).—The author has previously shown (Abstr., 1894, i, 289, 333, 464) that isomerides in the benzene series arrange themselves in pairs with respect to solubilities and some of their chemical properties. This holds good also in the case of melting and boiling points:—

*Dichlorobenzenes*, boiling points, *ortho* 179°, *meta* 172°, *para* 173°.

*Chloronitrobenzenes*, boiling points, *ortho* 243°, *para* 242°, *meta* 233°.

*Chlorotoluenes*, boiling points, *ortho* 156—157°, *meta* 156—157°, *para* 160—161°.

*Bromonitrobenzenes*, melting points, *ortho* 42°, *meta* 56°, *para* 126—127°.

*Diphenols*, melting points, *ortho* 104°, *meta* 110°, *para* 169°.

*Hydroxybenzoic acids*, melting points, *ortho* 155·5°, *meta* 200°, *para* 210°.

C. H. B.

**Stability of Halogen Derivatives of Benzene.** By C. Loring Jackson and Sidney Calvert (*Amer. Chem. J.*, 1896, **18**, 298—312).—1 : 3 : 5 : 2-Tribromiodobenzene, contrary to the statements of Silberstein (Abstr., 1883, 660), is less volatile than 1 : 3 : 5-tribromobenzene; it is most conveniently prepared by acting with hydriodic acid on the corresponding tribromodiazobenzene sulphate. When dissolved in benzene and heated with an alcoholic solution of sodium ethoxide during one hour, it is decomposed with production of 1 : 3 : 5-tribromobenzene together with a brownish-yellow powder, which melts above 300°, and is not completely soluble in any of the usual media. Hot sodium methoxide or cold sodium ethoxide effect only a partial decomposition of the substance, whilst sodium phenoxide, aqueous soda, sodium carbonate, moist zinc oxide, aniline, or ethylic sodiomalonate are without action; alcoholic soda, however, gives a large quantity of tribromobenzene. That the elimination of the iodine is due to the influence of the bromine atoms is shown by the stability of iodobenzene towards boiling alcoholic sodium ethoxide.

Iodine is liberated when cold fuming nitric acid is caused to act on 1 : 3 : 5 : 2-tribromiodobenzene, and the latter is converted into 1 : 3 : 5 : 2 : 4-tribromodinitrobenzene, $C_6HBr_3(NO_2)_2$, melting at 191°.

1 : 2 : 3 : 5-Tetrabromobenzene and 1 : 3 : 5 : 2-tribromochlorobenzene are slowly attacked by boiling sodium ethoxide, 1 : 3 : 5-tribromobenzene being produced as before, but in much smaller quantity, 1 : 2 : 4 : 5-tetrabromobenzene, under similar conditions, suffers partial conversion into 1 : 2 : 4-tribromobenzene.

The authors have convinced themselves of the correctness of Blau's observation (Abstr., 1887, 242) that symmetrical tribromobenzene is converted into dibromophenylic ethylic ether by sodium ethoxide, and find that this agent attacks tetrabromodinitrobenzene [$(NO_2)_2 =$ 2 : 4] giving the tribromonitroresorcinol diethyl ether first obtained, together with what was in all probability trinitrophloroglucinol triethyl ether, by acting on tribromotrinitrobenzene with sodium ethoxide (Abstr., 1891, 1024).

From the above data, the authors conclude that, whilst in respect to the loosening effect on substituting atoms or groups situated in the benzene nucleus, nitro-groups are more powerful than halogen atoms, yet the effect produced by a halogen, in the ortho- or para-position with regard to the group in question, is not inconsiderable. A satisfactory explanation of the curious decomposition of symmetrical tribromotrinitrobenzene is made possible on this supposition.

A. L.

***Cis-* and *Trans-*Modifications of Benzene Hexabromide.** By WILLIAM R. ORNDORF and V. A. HOWELLS (*Amer. Chem. J.*, 1896, **18**, 312—319).—Benzene hexabromide, as obtained by Meunier's method (Abstr., 1885, 1126), consists of the pure α-modification, but when prepared according to the directions of Matthews (Trans., 1893, **61**, 110) this is accompanied by β-benzene hexabromide; in the latter case, the substances may be separated by means of chloroform in which the β-compound is practically insoluble.

α-Benzene hexabromide forms monoclinic crystals, $a : b : c = 0·9938 : 1 : 0·5268$; $\beta = 69° 22'$ (compare Des Cloizeaux, *Ann. Chim. Phys.*, [6], **10**, 269).

β-Benzene hexabromide crystallises in the cubic system, and shows octahedral and rhombic dodecahedral forms. It is more sparingly soluble in chloroform, benzene, toluene, and metaxylene than the corresponding α-compound, and is nearly insoluble in alcohol and ether. When heated with alcoholic potash, it affords, quantitatively, unsymmetrical tribromobenzene. It melts and decomposes at 253°.

α-Benzene hexabromide is in all probability the *trans*-compound; it presents in its properties a complete analogy with the *trans*-hexachloride. The β-hexabromide is doubtless the *cis*-modification, although it differs in crystalline symmetry from the corresponding hexachloride.

A. L.

**Preparation of Paraethyltoluene. Two Isomeric Barium Salts of Paraethyltoluenesulphonic acid. Two Methylparaethylphenols.** By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1895, [3], **13**, 889—894).—The author describes the method of preparation of paraethyltoluene from parabromotoluene and ethylic iodide by Fittig's reaction. By heating the paraethyltoluene with 2½ times its weight of concentrated sulphuric acid on the water bath for four hours, and saturating with barium carbonate, two barium salts are obtained; one, the β-salt, crystallises with $3H_2O$ in needles, and is very soluble in water; the other, the α-salt, crystallises with $2H_2O$ in prisms, and is less soluble in water. He considers them to be derivatives of the two sulphonic acids [$Me : Et : SO_3H = 1 : 4 : 2$ and $1 : 4 : 3$].

By converting these barium salts into the corresponding potassium derivatives, and fusing with potash, the corresponding phenols are obtained. The α-phenol boils at 225·5—226·5° (corr.), has sp. gr. = 0·99665 at 21°, and is a caustic liquid, only slightly soluble in water. The β-phenol boils at 219·8—220·8° (corr.).

J. F. T.

**Cryoscopic Experiments with Salts of Phenols.** By HEINRICH GOLDSCHMIDT and OTTO GIRARD (*Ber.*, 1896, **29**, 1224—1242).—When the weak monobasic phenols, such as ordinary phenol, metacresol, thymol, and α- and β-naphthol are added to dilute caustic soda solution, they lower the freezing point of the latter. The extent of this lowering is such as would correspond with the complete electrolytic dissociation of the salts formed, and in some cases even exceeds this. Since, however, it is unlikely that the salts of these phenols should either be completely dissociated or hydrolysed to the extent required to account for these results, the phenomenon remains at present without explanation. More strongly acid phenols, such as orthonitrophenol, quinone-oxime, β-naphthaquinone-oxime, and hydroxyazobenzene, on the other hand, do not lower the freezing point of dilute caustic soda, but raise it, since the salts formed are dissociated to a less extent than caustic soda. The more strongly acid dibasic phenols, such as resorcinol, quinol, and dioximidoresorcinol also raise the freezing point of dilute caustic soda, but to a greater extent than might be calculated from the general equation $2Na + 2OH + XHH = 2Na + X + 2H_2O$, according to which the introduction of a single molecule of the dibasic phenol causes the disappearance of two hydroxyl ions. Catechol is much less acid than its isomerides, and chiefly forms the monosodium salt, its disodium salt being hydrolysed to a very large extent. The sodium salt of dioximidoresorcinol is dissociated to a much smaller extent than those of the dihydroxyphenols.

In the case of hydroxy-oximes, such as oximidoresorcinol, the oxime hydroxyl is the first to react. Oximidobenzeneazoresorcinol acts as a well-marked dibasic phenol, whilst the isomeric benzeneazoximidoresorcinol behaves as a monobasic phenol. A. H.

**Iodine Derivatives of Anisoïl. Migration of an Iodine Atom.** By FRÉDÉRIC REVERDIN (*Ber.*, 1896, **29**, 997—1005).—2-*Iodanisoïl* was prepared by the diazo-reaction from orthanisidine; it is a heavy oil, boiling at 239—240° under 730 mm. pressure. When it is nitrated at 0° with a mixture of fuming nitric and acetic acids, it yields 2 : 4-*iodonitranisoïl*, [$OMe : I : NO_2 = 1 : 2 : 4$], which melts at 95—96°; a red bye-product melting at 63—64° is also formed. This nitro-compound, when reduced with stannous chloride, yields 2 : 4-*iodanisidine*, which melts at 74—75°; the *platinochloride* melts at 207°, the *thiocarbamide* at 194—195°, and the *acetyl derivative* at 152—153°; it yields paranisidine when reduced with sodium amalgam in alcoholic solution, and can be converted by the diazo-reaction into 2 : 4-*diiodanisoïl*, which melts at 68—69°.

4-*Iodanisoïl*, prepared by the diazo-reaction from paranisidine, melts at 51—52°, and boils at 237° under 726 mm. pressure. When nitrated it yields, in addition to a yellow substance (4 : 2-iodonitroanisoïl?) melting at 73°, and a substance melting at 87°, 2 : 4-iodonitroanisoïl, in all respects identical with the substance obtained from 2-iodanisoïl. The identity was further proved by crystallographic examination of the picrates of the two iodanisidines obtained by reducing the two samples; the two picrates were found to be identical, and to crystallise in the rhombic system ($a : b : c = 1·7800 : 1 : 0·5265$). A migration of the iodine atom from the 4 to the 2 position must thus have taken place during the nitration.

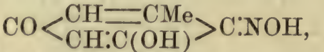
These iodo-compounds have no very marked physiological action.

The ortho- moniodo-compounds are more powerful antiseptics and local irritants than are those with the iodine in the para position. A second iodine atom weakens the effect. C. F. B.

**Action of Sodium on Phenylic γ-Bromopropylic Ether.** By Basil M. Solonina (*J. Russ. Chem. Soc.*, 1894, **26**, 1—5).—*Phenylic γ-bromopropylic ether*, $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}OPh$, was obtained by the action of an excess of trimethylene bromide on sodium phenoxide, the ether being distilled under a pressure of 200 mm., when it boiled at 211—212°; 35 per cent. of the theoretical quantity was obtained. The sp. gr. of the ether = 1·365 at 16°/16°. It was added to metallic sodium under a layer of absolute ether, taking care to keep the mixture cool; after some days, the solution was filtered from the sodium bromide and sodium phenoxide, treated with water, the ether distilled off, and the residue recrystallised from 95 per cent. alcohol. The substance obtained in this way melts at 83°; the long, needle-shaped crystals are very soluble in ether, benzene, and chloroform, fairly so in hot 95 per cent. alcohol, but only sparingly in cold alcohol. The analysis gave numbers corresponding with the formula $C_6H_{12}(C_6H_5O)_2$, which is that of the diphenylic ether of hexamethyleneglycol. This was confirmed by a molecular weight determination by Raoult's method. The corresponding iodide and bromide, $C_6H_{12}I_2$ and $C_6H_{12}Br_2$, were obtained from it by the action of hydriodic and hydrobromic acids.

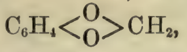
S. G. R.

**Two Modifications of Mononitroso-orcinol [Oximido-orcinol].** By Fr. Henrich (*Ber.*, 1896, **29**, ii, 989—993).—Krämer (Abstr., 1884, 1340) and Nietzki and Mackler (Abstr., 1890, 763) have prepared two modifications of monoximido-orcinol,



$$\mathrm{CO}<\begin{matrix}\mathrm{CH{=\!=}CMe}\\ \mathrm{CH{:}C(OH)}\end{matrix}>\mathrm{C{:}NOH},$$

without noticing the fact. Their method of preparation was adopted, except that the potassium, instead of the sodium, derivative was prepared. If a hot aqueous solution (1 : 10) of this substance is treated with boiling, dilute sulphuric acid (1 : 3), and the mixture allowed to cool, dark red crystals are formed. If an aqueous solution (1 : 12) is cooled with ice and treated with dilute sulphuric acid, an orange-red, flocculent precipitate is momentarily formed, but this changes at once into a yellow powder. The red substance carbonises at 110—112° when impure, but when pure it is transformed at 100—110° into the yellow variety, and then turns brown at 157—162°, finally melting, or occasionally exploding. The red substance is monoclinic and strongly dichroïc, whereas the yellow variety is not dichroïc and is optically uniaxial—probably tetragonal. The yellow (α) variety is the stable one, and is formed from the red variety (β), when a current of hot air is passed over the latter; it is possible, however, to effect a partial transformation of the yellow into the red variety, by boiling down a solution in some solvent that boils under 100°, such as acetone. It is difficult to say what is the nature of the isomerism of the two substances, for they yield identical derivatives; namely, when reduced, a base with the hydrochloride $C_7H_7O_2{\cdot}NH_2,HCl + 2H_2O$; when nitrated, a dinitro-orcinol melting at 164—165°; and with acetic anhydride, an *acetyl derivative*, $C_7H_6AcNO_2 + 2H_2O$, which softens at 115°, and melts at 119—120°. C. F. B.

**Safrole and Isosafrole.** By CHARLES MOUREU (*Compt. rend.*, 1896, **122**, 792—795).—Methylenecatechol [orthomethylenedioxybenzene],  $C_6H_4<\begin{smallmatrix}O\\O\end{smallmatrix}>CH_2$, obtained by the action of methylene iodide on disodium catechol, is an oily, colourless liquid which has an aromatic odour, and boils at 172—173°; sp. gr. = 1·202 at 0°. When treated with allylic iodide and zinc powder, it would doubtless yield safrole.

If isosafrole really has the constitution usually attributed to it, it ought to be formed by the action of heat on methylenebromocaffeic acid (Lorenz, Abstr., 1881, 48). The latter is prepared by the interaction of piperonal, propionic anhydride, and dry sodium propionate, and crystallises from alcohol in small needles, which melt at 198—199°. The silver salt crystallises from boiling water in slender, white needles. When carefully heated, the methylenebromocaffeic acid begins to decompose at 270°, and yields isosafrole amongst other products. Much larger quantities are, however, formed by the decomposition of part of the methylenecaffeic acid during its preparation by the reaction indicated. The isosafrole thus obtained is identical with the natural product. These results establish the constitution usually attributed to safrole and isosafrole; the former is allylmethylenecatechol, and the latter propenylmethylenecatechol.

C. H. B.

**Isosafrole Nitrosite.** By ANGELO ANGELI and ENRICO RIMINI (*Gazzetta*, 1896, **26**, i, 7—12).—The isosafrole nitrosite first prepared by Angeli (Abstr., 1892, 447), readily loses water, yielding a dioxime peroxide (Abstr., 1892, 1198), and, on heating with water, alcohol, or, better, piperidine, it also loses water yielding a *compound*, $C_{10}H_9NO_4$, which is precipitated on passing carbonic anhydride through the piperidine solution; it is a yellow, crystalline substance melting at 98°. The aqueous mother liquors obtained during its recrystallisation subsequently deposit a white substance melting at 134°; this is an additive *compound* with piperidine, having the composition $C_{10}H_9NO_4,C_5H_{11}N$.

On heating isosafrole nitrosite with primary bases such as aniline, resinous products are obtained, but on dissolving it in alcoholic benzylamine solution, heat is developed, and a white crystalline *product*, which melts at 76°, may be precipitated from the solution by adding water; it yields benzylamine hydrochloride and piperonal on treatment with dilute hydrochloric acid, and consequently has the constitution $CH_2O_2{:}C_6H_3{\cdot}CH{:}N{\cdot}CH_2Ph$.

Similarly, on boiling isosafrole nitrosite with alcoholic hydroxylamine hydrochloride and soda, piperonaloxime, melting at 110—112°, is obtained.

The compound of the composition $C_{10}H_9NO_4$ described above would, on the basis of the above results, seem to be piperonyl-β-nitropropylene $CH_2O_2\colon C_6H_3\cdot CH\colon CMe\cdot NO_2$, and its hydrolysis by alkalis should occur in accordance with the equation
$CH_2O_2\colon C_6H_3\cdot CH\colon CMe\cdot NO_2 + H_2O = CH_2O_2\colon C_6H_3\cdot COH + CH_2Me\cdot NO_2$; the authors were, however, unable to detect nitroethane amongst the products of hydrolysis. W. J. P.

**Action of Acid Chlorides on the Silver Salts of the Anilides.** By HENRY L. WHEELER and B. B. BOLTWOOD (*Amer. Chem. J.*, 1896, **18**, 381—389).—*Benzoformanilide*, $CHO\cdot NPhBz$, is prepared by adding benzoic chloride (1 mol.) to dry silver formanilide (1 mol.) suspended in benzene; it crystallises in colourless needles, melts at 112°, and dissolves readily in benzene and chloroform, less so in ether and alcohol, and with difficulty in water; treatment with sodium hydroxide removes the formyl group, yielding benzanilide.

2 : 4-*Dichloroformanilide* was prepared by chlorinating acetanilide according to the method of Beilstein and Kurbatow (*Annalen*, **196**, 215), and replacing the acetyl group by the formyl group in the usual manner. It crystallises in colourless needles, and melts at 153°. The *silver* compound, $C_6H_3Cl_2\cdot NAg\cdot CHO$, is described; by treating this with benzoic chloride, *benzoformo*-2 : 4-*dichloranilide* is obtained; it crystallises in prisms, melts at 77°, and dissolves readily in benzene and hot alcohol, but only sparingly in water.

*Benzo*-2 : 4-*dichloranilide*, formed by boiling formobenzo-2 : 4-dichloranilide with hydrochloric acid, melts at 117°, and dissolves sparingly in hot water, but freely in hot alcohol and ether.

*Benzoformorthotoluidide*, prepared like benzoformanilide, crystallises in thick rectangular plates, melts at 92°, and dissolves freely in benzene and warm alcohol, but with difficulty in water; treatment with sodium hydroxide converts it into benzorthotoluidide.

Silver formanilide and ethylic chlorocarbonate react to form, among other products, ethylisoformanilide (Comstock and Clapp, Abstr., 1892, 707) which, when mixed with 2 : 4-dichloraniline, yields *phenyl*-2 : 4-*dichlorophenylformamidine*, $NPH\colon CH\cdot NH\cdot C_6H_3Cl_2$; this crystallises in aggregates of colourless plates, and melts at 159°. *Ethylic orthotolylformimido-ether*, $C_6H_4Me\cdot N\colon CH\cdot OEt$, is an aromatic oil, boiling at 101° under a pressure of 12 mm. A. G. B.

**Nitration of Dimethylparatoluidine.** By PIETER VAN ROMBURGH (*Ber.*, 1896, **29**, 1015—1016).—Pinnow's contention (this vol., i, 161) that the author's method does not give a homogeneous product is incorrect. In the first place, the author did not dissolve his dimethylparatoluidine in acetic acid, and in the second, even if this is done, a homogeneous product can be obtained quite easily.

The dinitrotolylmethylnitramine formed is converted by boiling with a little phenol into dinitromethyltoluidine. This, when heated with sodium nitrite in nitric acid solution, yields dinitrotolylmethylnitrosamine; and this exchanges its nitroso-group for a nitro-group when boiled with fuming nitric acid, and for hydrogen when boiled with phenol. C. F. B.

**Action of Propylic, Butylic, and Amylic Sodiocyanacetates on Diazobenzene Chloride.** By G. Favrel (*Compt. rend.*, 1896, **122**, 844—846).—The direct action of propylic, butylic, and amylic sodiocyanacetates on diazobenzene chloride yields the corresponding benzeneazocyanacetates, $Ph{\cdot}N_2{\cdot}CH(CN){\cdot}COOR$. These are obtained in the $\alpha$-modification by crystallisation from light petroleum, and in the $\beta$-modification by treating the former in different ways.

*Propylic Benzeneazocyanacetate.*—The $\alpha$-modification forms slender, pale yellow needles, melts at 78—80°, and is converted into the $\beta$-modification by melting, and crystallising from hot, light petroleum. The latter forms elongated yellow prisms, and melts at 102—103°. When crystallised from strong solutions or from cold benzene, the crystals are rhomboïdal or hexagonal plates with the same melting point.

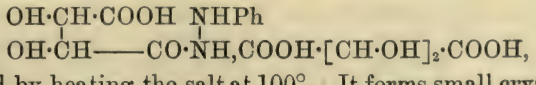
*Butylic Benzeneazocyanacetate.*—The $\alpha$-modification forms very light, silky, pale yellow needles, which melt at 118—120°. When dissolved in sodium hydroxide, and precipitated by carbonic anhydride, it is converted into the $\beta$-modification, which crystallises from benzene in pale yellow prisms melting at 98—101°.

*Amylic Benzeneazocyanacetate.*—The $\alpha$-modification crystallises from light petroleum in very pale, yellow needles, which melt at 77—78°, but if boiled for some time, the solution, on cooling, deposits the $\beta$-modification in yellow prisms, which melt at 57—59°.

It will be seen that the propyl-, butyl-, and amyl-sodiocyanacetates behave in the same way as their lower homologues, and it is noteworthy that the melting point of the product (except in the case of the butylic derivatives) decreases from methyl to amyl in the case of both the $\alpha$- and $\beta$-modifications. C. H. B.

**Phenylhydrazine Tartrate and its Derivatives.** By Henri E. Causse (*Compt. rend.*, 1896, **122**, 940—942).—Phenylhydrazine hydrogen tartrate is obtained in colourless, prismatic needles by adding 100 grams of phenylhydrazine to a solution of 100 grams of tartaric acid in 500 c.c. of strong alcohol, and then adding to the liquid its own volume of ether at 65°. The product is purified by crystallisation from boiling alcohol; it melts and decomposes at 118—119°, and is somewhat feebly lævogyrate. The hydrogen tartrate most probably has the constitution $H{\cdot}C_4H_6O_6{\cdot}NPh{\cdot}NH{\cdot}C_4H_6O_6{\cdot}H$; it behaves as a dibasic acid towards bases, and forms an amido-derivative and a hydrochloride. The potassium salt forms small, white crystals only slightly soluble in cold water, and insoluble in alcohol and ether, the aqueous solution being lævogyrate; the barium salt forms white, microscopic crystals, and its aqueous solution is lævogyrate; the antimonyl (SbO) salt forms small, silky crystals, soluble in water, but less soluble in alcohol, both solutions being lævogyrate.

The amido-derivative,



$$\begin{array}{l} \mathrm{OH{\cdot}CH{\cdot}COOH\quad NHPh} \\ \qquad\ \ | \qquad\qquad\qquad\quad\ \ | \\ \mathrm{OH{\cdot}CH{-\!\!-\!\!-}CO{\cdot}NH,COOH{\cdot}[CH{\cdot}OH]_2{\cdot}COOH,} \end{array}$$

is obtained by heating the salt at 100°. It forms small crystals, which melt at 225°, and are only slightly soluble in water and alcohol, but the solutions are more strongly lævogyrate than those of the hydrogen tartrate.

The hydrochloride is obtained by the direct action of hydrochloric acid, and forms small crystals, the solutions of which are lævogyrate. A benzoic and an aldehydic derivative have also been prepared.

C. H. B.

**Behaviour of Opianic acid and its Ethereal Salts with Reagents for Aldehydes.** By Rudolf Wegscheider (*Monatsh.*, 1896, **17**, 111—120; compare Abstr., 1895, i, 420, and Liebermann, this vol., i, 232).—With a solution of magenta decolorised with sulphurous acid, the acid itself gave little or no red coloration, the true methylic salt a red colour, and the ψ-methylic salt no colour.

With diazobenzeneparasulphonic acid, potash solution and 4 per cent. sodium amalgam, all three give a violet-red coloration, that with the acid is the strongest, the true methylic salt comes next, and the ψ-salt is weakest.

By treating opianic acid with pyruvic acid and β-naphthylamine, Liebermann's β-naphthylamide of opianic acid is formed; this melts at 207—207·5° (Liebermann gives 213°), and is almost insoluble in ether and hot water. Doebner's α-methyl-β-naphthocinchoninic acid (Abstr., 1894, i, 261, 532) is formed at the same time; it melts at 290° (Doebner gives 310°).

Both the acid and ψ-methylic salt give meconine when reduced with acetic acid and zinc dust; the acid and both salts, with hydroxylamine, yield opianoximic acid anhydride (compare Liebermann, Abstr., 1887, 258). The action of phenylhydrazine on the three compounds is also given (compare Liebermann, Abstr., 1886, 550).

J. J. S.

**Two Orthophthalic acids.** By W. T. H. Howe (*Amer. Chem. J.*, 1896, **18**, 390—401).—The variation in the melting point of phthalic acid as determined by different observers is due to the existence of two isomeric forms of the acid, distinguished in this paper as α-phthalic acid, which melts at 203°, and β-phthalic acid, which melts at 184°. Commercial phthalic acid is generally a mixture of the two, and when its aqueous solution is boiled for three to four hours, the α-acid crystallises out on cooling. Graebe's observation that the acid melts at 183—184°, if kept at this temperature for some time, is due to the formation of anhydride. The β-acid may be prepared in a pure condition by dissolving phthalic anhydride in cold dilute sodium hydroxide, cooling to 0°, slowly precipitating by hydrochloric acid, and drying the precipitate over sulphuric acid. Phthalic anhydride appears, therefore, to be derived from the β-acid. The α-acid yields the β-form when boiled with a 30 per cent. solution of sodium or potassium hydroxide for four or five hours, and then precipitating and drying as just described; the conversion is also partially effected by strong acids. The β-acid is very sensitive to warm water, easily becoming partially converted into the α-acid, but for complete conversion three or four hours' boiling is essential. Light has no effect on the β-acid. Melting points lower than that of the β-acid, observed by some investigators, are ascribed to the contamination of their specimens by acid salts.

The molecular refraction of the acids is virtually identical, but the electrical conductivity of the α-acid is lower than that of the β-acid. 100 parts of absolute alcohol at 20° dissolve 11·74 parts, and at 23° 14·08 parts of the α-acid, whilst the same quantity of solvent dissolves 14·12 parts of the β-acid at 20°, and 16·18 parts at 23°.

The following table shows the differences between some salts of the two acids.

| Salt. | α-acid. | β-acid. |
|---|---|---|
| Aniline.......... | Plates, m. p. 160° | Plates, m. p. 147—148° |
| α-Naphthylamine. | Prisms, m. p. 163° | Needles, m. p. 155° |
| Quinoline........ | Plates, m. p. 98° | Needles, m. p. 92° |
| Brucine......... | Prisms, m. p. 228° | Needles, m. p. 212—313° |

Warm alcohol or an excess of the base quickly changes the salts of the β-acid into those of the α-acid.

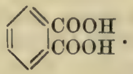
By reduction with sodium amalgam, the β-acid yields a dihydro-acid which differs in the following respects from the $\Delta_{3\cdot5}$ acid obtained by Baeyer, from the α-acid.

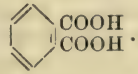
| | $\Delta_{3\cdot5}$ acid. | New dihydro-acid. |
|---|---|---|
| Melting point ........... | 210° | 195° |
| ,, ,, of anhydride | 101—103° | 126 |
| With cold solution of $AgNO_3$............... | No reaction. | Reduces. |
| With sodium amalgam in the cold.............. | No reaction. | Reduces to tetrahydro-acids. |
| With cupric acetate...... | Precipitation of cuprous oxide on addition of acetic acid. | Precipitation of cuprous oxide without addition of acetic acid. |

Of the two tetrahydro-acids prepared by reducing the new dihydro-acid, one is the $\Delta^1$-tetrahydrophthalic acid (m. p. 120°), prepared by Baeyer, the other is a new acid, and melts at 206°.

Several metallic salts of α- and β-orthophthalic acids have been prepared; in many cases they differ in form and in their content of water of crystallisation. The α-salt is more stable than the β-salt, and the latter is converted into the former by boiling with water.

The author is of opinion that these acids are cases of the single and double bond isomerism required by Kekulé's benzene formula, and heretofore regarded as a stumbling-block to the acceptance thereof. The acids would be represented by the formulæ





A. G. B.

**Transformations of Parasulphaminebenzoic acid when heated.** By Ira Remsen and Arthur M. Muckenfuss (*Amer. Chem. J.*, 1896, **18**, 349—365).—When parasulphaminebenzoic acid is heated for three hours at 285°, the mass becomes coloured, and is freely soluble in water and alcohol, but not in benzene, ether, and light petroleum. The aqueous solution contains ammonium hydrogen parasulphobenzoate almost exclusively; in view of this fact, and that there is no loss of weight when the acid is heated, the authors believe that the ammonium salt is formed by the hydrolysis of benzaminesulphonic acid, $NH_2\cdot CO\cdot C_6H_4\cdot SO_3H$, which may be supposed to constitute the immediate product of the action of heat on parasulphaminebenzoic acid, $COOH\cdot C_6H_4\cdot SO_2\cdot NH_2$, having been formed by a migration of the nitrogen atom analogous to that which occurs in the conversion of ammonium cyanate into urea or that of benzildioxime into oxanilide (compare this vol., i, 372).

When heated at 220—235° for eight hours, and then treated with water, parasulphaminebenzoic acid yields an insoluble compound which may be purified by dissolution in dilute caustic soda, treatment in the cold with animal charcoal, and acidification with hydrochloric acid, which causes the separation of characteristic crystals of the new compound. This substance is infusible, and, since its analysis gives figures which agree with the formula

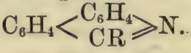
$$NH_2\cdot SO_2\cdot C_6H_4\cdot CO\cdot NH_2,$$

and its properties indicate that it is an amide, it is referred to as the infusible diamide. It does not dissolve in any of the usual solvents; strong sulphuric acid dissolves it readily, and when the solution is diluted the infusible diamide is precipitated in small plates, even though the solution has been heated to 200°. It is unchanged by heating with phosphorus pentachloride at 200° for several hours; concentrated hydrochloric acid at 200° converts it into ammonium hydrogen parasulphobenzoate and ammonium chloride, a small quantity of an insoluble compound being formed at the same time. The infusible diamide loses the whole of its nitrogen as ammonia when treated with caustic soda, even at low temperatures.

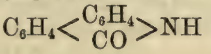
To compare the properties of this supposed diamide with that of the diamide of parasulphobenzoic acid, the latter was prepared in the usual manner; it dissolves readily in boiling water and in alcohol; it melts sharply at 230°. The action of hydrochloric acid on this diamide is similar to that of the acid on the infusible diamide; sodium hydroxide expels half the nitrogen from the fusible diamide, producing parasulphaminebenzoic acid.

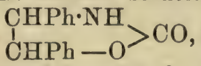
The aqueous solution of the product obtained by heating parasulphaminebenzoic acid at 220—235°, filtered from the insoluble diamide, contains ammonium hydrogen parasulphobenzoate, parasulphobenzoic acid, and a compound intermediate in solubility between these two, and called *isoparasulphaminebenzoic acid.* The *barium* salt of this acid crystallises in sparingly soluble needles, with $3H_2O$, remarkable for the manner in which they fill the mother liquor. The free acid is very soluble in water; it gives up its nitrogen with difficulty when heated with potassium hydroxide solution, a fact at variance with the supposition that the acid may be benzaminesulphonic acid, since this would contain a $CONH_2$ group which is known to easily lose nitrogen as ammonia. Isoparasulphaminebenzoic acid is less easily attacked by hydrochloric acid than is parasulphaminebenzoic acid, but yields the same products; attempts to prepare the amide were not successful.

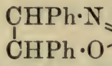
This investigation is being continued. A. G. B.

**New Synthesis of Phenanthridine Bases.** By Amé Pictet and A. Hubert (*Ber.*, 1896, **29**, 1182—1189).—When orthamidodiphenyl (Abstr., 1894, i, 529) is treated with the anhydride of a fatty acid or with benzoic chloride, a derivative, $C_6H_5\cdot C_6H_4\cdot NH\cdot CRO$, is formed, and this, when heated with 3—4 times its weight of zinc chloride at 250—300°, yields a phenanthridine,  $C_6H_4\!<\!\genfrac{}{}{0pt}{}{C_6H_4}{CR}\!\geqslant\!N$. These phenanthridines were purified by precipitation as mercurichlorides; the phenyl compound, however, by crystallising the hydrochloride. They are colourless, and form colourless salts with colourless acids; the aqueous solutions of salts with mineral acids, except those of the phenyl derivative, exhibit a faint blue fluorescence. Phenanthridine itself (Abstr., 1890, 390) and its methyl, ethyl, and phenyl derivatives were prepared by this method. In the following list of new compounds described, the numbers indicate melting points (often points of decomposition, also, in the case of salts), except where the contrary is stated.

*Formamidodiphenyl*, 75°. Acetamidodiphenyl, 117°; boils at 335° (uncorr.). *Propionamidodiphenyl*, 65°; boils about 350°. *Benzamidodiphenyl*, 85—86°. *Methylphenanthridine*, 85°; boils above 360°: *hydrochloride*, 285°; *platinochloride* (with $2H_2O$), flesh-coloured, 272°; *aurochloride*, yellow, 163—164°; *mercurichloride*, 247°; *picrate*, yellow, 233°; *methiodide*, 246—247°. *Ethylphenanthridine*, 54—55°: *hydrochloride*, 205°; *platinochloride*, with $2H_2O$, yellow, 241—242°; *aurochloride*, yellow, 149°; *mercurichloride*, 214°; *picrate*, yellow, 210°. *Phenylphenanthridine*, 109°; boils above 400°: *hydrochloride* (with $H_2O$) melts at 95—96°, then solidifies, and melts again at 220°; *nitrate*, 205°; *platinochloride*, with $2H_2O$, yellow; *mercurichloride*, yellow (?), 220°; *picrate*, yellow, 242°.

Ethylic chloroformate acts on orthamidodiphenyl, forming *diphenylurethane*, $C_6H_5\cdot C_6H_4\cdot NH\cdot COOEt$. This melts at 186°, and yields phenanthridone,  $C_6H_4\!<\!\genfrac{}{}{0pt}{}{C_6H_4}{CO}\!>\!NH$ (Abstr., 1893, 658), when heated with zinc chloride. C. F. B.

**Condensation Products of Hydroxydiphenylethylamine.** By Henrik G. Söderbaum (*Ber.*, 1896, **29**, 1210—1216; compare Abstr., 1895, i, 596).—Carbonyl chloride reacts with diphenylhydroxyethylamine in toluene solution to form 4 : 5-*diphenyl*-2-*ketodihydro*-1 : 3-*azoxole*,  $\begin{array}{l}CHPh\cdot NH\\ \mid\\ CHPh-O\end{array}\!\!>CO$, which crystallises in slender, matted needles melting at 189—189·5°. It is insoluble in dilute acids and alkalis. *Hydroxydiphenylethylurethane*, $OH\cdot CHPh\cdot CHPh\cdot NH\cdot COOEt$, is formed by the action of ethylic chloroformate on the same base. It crystallises in colourless needles melting at 148—148·5°, and is converted at 275° into the foregoing compound, with elimination of ethylic alcohol. Carbon bisulphide converts the diphenyl base into 4 : 5-*di*-

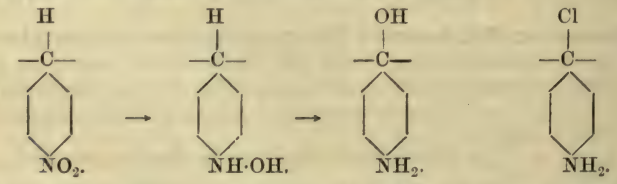
*phenyl-2-thiodihydro-*1 : 3-*azoxole*,  $\begin{matrix}\text{CHPh·N}\\ | \\ \text{CHPh·O}\end{matrix}\!\!>\!\text{C·SH}$, which crystallises in stellate groups of tablets, and melts at 185°. This compound has distinct acid properties, and dissolves in cold, dilute aqueous soda. It is readily attacked by oxidising agents. *Hydroxydiphenylethylamine formate* crystallises in white, nacreous plates, which melt and decompose at 182°. *Formylhydroxydiphenylethylamine*, $C_{14}H_{14}NO·CHO$, is obtained by heating the foregoing substance, and crystallises in needles which melt at 182—183°. The *diformyl* derivative is prepared by the continued action of formic acid on the base, and forms vitreous needles which melt at 208°. *Acetylhydroxydiphenylethylamine* melts at 196—197°; the *diacetyl* derivative crystallises in short, four-sided prisms, and melts at 212—213°. The isomeric diacetyl derivative, which is stated by Goldschmidt and Polonowska to melt at 159° (Abstr., 1887, 492), does not appear to exist. *Acetylisohydroxydiphenylethylamine* melts at 152—153°. *Benzoylhydroxydiphenylethylamine* forms slender, matted needles, and melts at 236—237°; the *dibenzoyl* derivative melts at 254°. This compound is accompanied by about 26 per cent. of *dibenzoylisohydroxydiphenylethylamine*, which melts at 186—187°. Since the original base was free from iso-compound, it appears that partial molecular change must occur under the influence of the benzoic chloride which is used for the preparation.

A. H.

### Reduction of Nitrotetramethyldiamidotriphenylmethane.

By Maurice Prud'homme (*Bull. Soc. Chim.*, 1895, [3], **13**, 913—915). —When nitrotetramethyldiamidotriphenylmethane is reduced by means of zinc dust and hydrochloric acid, the curious fact is noticed that, if the acid is in excess, a violet colouring matter, capable of dyeing cotton mordanted with tannin, silk, or wool, is directly produced, without any subsequent oxidation.

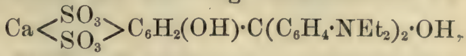
This the author explains in the following way. The nitro-group is first reduced to NH·OH, and the action of hydrochloric acid on this group tends to make the hydroxyl migrate to the para-position in the benzene nucleus. This position is, however, already occupied, it therefore takes the place of the hydrogen in the methyl group, which can be regarded as opposite to the group NH·OH.



The further action of hydrochloric acid converts this into the coloured salt.

In support of this theory, the author has succeeded in isolating the phenylhydroxylamine, which, on treatment with hydrochloric acid, yields the violet colouring matter.

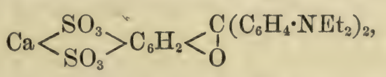
J. F. T.

**Sulphonated Colouring Matters of the Triphenylmethane Series. "Patent Blue."** By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1895, [3], **13**, 905—913).—From the following considerations the author inclines to the formula  $\mathrm{Ca}<\substack{SO_3\\SO_3}>C_6H_2(OH)\cdot C(C_6H_4\cdot NEt_2)_2\cdot OH$, for the dye "Patent blue." (1) The dye does not precipitate barium chloride, and therefore does not contain the acid radicle directly combined to the methane carbon atom, as in the case of the sulphates of rosaniline and similar bases. (2) In the hydrolysis with sodium hydroxide, no sodium sulphate is produced. (3) It decomposes ammonium salts in the cold, and therefore contains hydroxyl directly combined with the methane carbon atom.

The alkaline solution, after being decolorised by sodium hydroxide and exactly neutralised in the cold, becomes re-coloured slowly on standing in the cold, but quickly on warming. The re-coloration is, therefore, not due to etherification but to simple hydrolysis.

"Patent blue" is only decolorised by a concentrated solution of sodium hydroxide after standing some days. After prolonged boiling, decomposition ensues, diethylamine vapour being evolved, and a sulphonated aurine produced; this substance is characterised by having the hydroxyl groups in the *meta*- instead of the *para*-positions. It is closely analogous to ordinary aurine, dyeing silk a pale yellow.

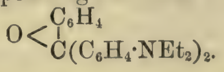
The solution of "Patent blue" decolorised by sodium hydroxide in the cold, shows the following properties. (1) Diluted with water and warmed on the water bath with zinc dust for from 5 to 10 hours, it regenerates the leuco-derivative of the blue. (2) On being made acid with excess of acetic acid and treated with lead peroxide, it yields tetrethylbenzidine. From these data, coupled with the fact that the original colouring matter is regenerated from the decolorised solution on standing, and therefore by hydrolysis, the author considers the formula of the decolorised compound to be



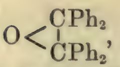
$$\mathrm{Ca}<\substack{SO_3\\SO_3}>C_6H_2<\substack{C(C_6H_4\cdot NEt_2)_2,\\ | \\ O}$$

that is to say, the action of the sodium hydroxide has effected a condensation with elimination of water.

An analogy is also drawn between "Patent blue" and "Helvetia green," the difference between them being merely that the former contains an additional hydroxyl in the *meta*-position. The base of "Helvetia green" shows the same reactions as the "Patent blue." It is decolorised by sodium hydroxide, slowly in the cold, rapidly on warming. On standing the colour reappears. With lead peroxide in a solution of acetic acid, tetrethylbenzidine is produced.

The corresponding formula for this decolorised compound would therefore be  $O<\substack{C_6H_4\\ | \\ C(C_6H_4\cdot NEt_2)_2}$.

J. F. T.

**Triphenylethanone and Triphenylethanolone.** By MAURICE DELACRE (*Bull. Soc. Chim*,, 1895, [3], **13**, 857—862).—The author has for some years held the view that benzopinacoline has the symmetrical formula  $O<\begin{matrix}CPh_2\\ |\\ CPh_2\end{matrix}$, and not the ketonic formula $CPh_3{\cdot}COPh$, usually applied to it. He has therefore attempted to prepare the latter compound, but without success. By the action of benzene on trichloracetic chloride in the presence of aluminium chloride, only *triphenylethanone* (diphenylacetophenone), $CHPh_2{\cdot}COPh$, is produced. This substance, already prepared by Saint-Pierre, crystallises from acetic acid in white needles, melting at 135°, and distilling at 270—280° (40 mm.). It combines with hydroxylamine only under certain conditions, and does not appear to yield a hydrazone. It has a negative hydrogen atom, readily replaceable by metals of the alkali group; the resulting compound does not, however, combine with bromobenzene with the formation of the tetraphenyl derivative sought for. The *bromo-derivative*, $CPh_2Br{\cdot}COPh$, is prepared by adding the calculated quantity of bromine to a solution of the triphenylethanone in carbon bisulphide. It crystallises from light petroleum in slender, transparent needles, melting at 97°. Attempts to substitute a phenyl group for the bromine atom by Friedel and Craft's reaction were unsuccessful, the compound being simply reduced.

*Triphenylethanolone*, $OH{\cdot}CPh_2{\cdot}COPh$ (diphenylhydroxyacetophenone), is produced by acting directly on triphenylethanone with bromine, and separating the product with water. It forms silky tufts melting at 84°. The *acetate* forms fine, vitreous crystals, melting at 145—146°. J. F. T.

**Isomeric Acetylaurins.** By JOSEF HERZIG (*Monatsh.*, 1896, **17**, 191—198; compare Herzig and von Smoluchowski, Abstr., 1894, i, 336).—From the alcoholic mother liquor obtained in the preparation of acetylaurin (*loc. cit.*), the author has isolated a substance which melts at 146—149°, and is isomeric with acetylaurin. Both acetyl derivatives when hydrolysed yield aurin, and this, when again acetylated, gives a mixture of the two acetyl derivatives. The isomeride of low melting point is readily converted into that of higher melting point by dissolving it in acetic acid, and allowing the solution to remain for some time. The author thinks this isomerism is similar to the isomerism observed by Baeyer among the hydrophthalic acids.

J. J. S.

**Peridinitronaphthalene.** By CH. GASSMANN (*Ber.*, 1896, **29**, 1243—1246).—The author describes several methods of nitrating naphthalene with the object of obtaining the best yield of 1 : 1′-dinitronaphthalene. The largest amount, 67·9 of the theoretical yield, is obtained by bringing 128 grams of naphthalene in the cold into a mixture of 260 grams of nitric acid of 61·7 per cent. with 300 grams of 92 per cent. sulphuric acid and 200 grams of fuming sulphuric acid containing 60 per cent. of anhydride. After shaking well, the whole is heated for 12 hours on the water bath. The 1 : 1′-compound is then extracted from the mass by acetone, and recrystallised.

A. H.

**Derivatives of the Naphthylamines.** By CARL BOETTINGER (*Arch. Pharm.*, 1896, **234**, 170—185; 185—194; compare Abstr., 1895, i, 106).—*Mono-β-naphthylamine succinate* is the only product formed when β-naphthylamine and succinic acid are dissolved in alcohol. It crystallises in slightly brownish needles, melts at 132—133°, and is partially decomposed by boiling with water.

*Succino-β-naphthalide*, $C_2H_4(CO\cdot NH\cdot C_{10}H_7)_2$, which is obtained by heating the base with succinic acid, crystallises in very small needles, is only sparingly soluble in boiling alcohol, and melts at 264°. Acetic anhydride does not yield an acetyl derivative, but converts it into *succino-β-naphthil*, $C_2H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot C_{10}H_7$, which forms prismatic crystals, melts at 176°, but solidifies again at a few degrees above this temperature, and then melts again at 183—184°.

*Pyruvic-β-naphthil* is formed along with a little dinaphthylamine when pyruvic acid is heated with β-naphthylamine; it crystallises in rosettes of small prisms, and melts at 158—159°.

Glycollic-α-naphthalide is converted by benzoic chloride into a *benzoyl* derivative, which crystallises in broad needles melting at 191—191·5°. *Glycollic-β-naphthalide* crystallises in large, colourless prisms, and melts at 138—139°. The *benzoyl* derivative forms needles, which melt at 163°. An acetyl derivative could not be obtained.

*Normal β-naphthylamine tartrate* crystallises in large, white plates, with a silvery lustre, and melts at 170—171°.

*Tartaric-β-naphthalide* is a white powder, which is almost insoluble in alcohol, and melts at 264—265°. Acetic anhydride converts it into *acetyltartaric-β-naphthalide*, which melts at 229—230°, and *diacetyltartaric-β-naphthalide*, which crystallises in compact, hard prisms, and melts at 226°.

When molecular proportions of citric acid and β-naphthylamine are mixed in alcoholic solution, *mono-β-naphthylamine citrate* crystallises out in silky needles, melting at 92°. When 2 mols. of the base are mixed with one of the acid, on the other hand, an *isomeric salt*, which melts at 138°, but resembles the first in appearance, is formed. When 3 mols. of the base are employed, an *additive compound* of the mononaphthylamine salt, with 4 mols. of base, is formed. This crystallises in white chalk-like masses, melts at 114°, and readily loses β-naphthylamine at a higher temperature. When citric acid is heated with β-naphthylamine, the *anhydride* of *citric-di-β-naphthalide* is produced along with the *β-naphthylamine salt* of *citric-dinaphthalide*. The former of these is obtained in small, hard crystals, melting at 235—236°. When boiled with acetic anhydride for some time, it is converted into a yellowish, crystalline powder, which melts at 192°, and gives an intense yellowish-red coloration with alcoholic soda. The β-naphthylamine salt of citric dinaphthalide is a greyish-yellow powder, melting at 150—151°.

When succino-β-naphthil is boiled with alcoholic soda, it yields the sodium salt of *β-naphthalidosuccinic acid*. The free acid crystallises in long, lustrous needles or broad plates, and melts at 181—182°. The *calcium salt* forms slender needles, whilst the *barium salt* crystallises in compact needles. *β-Naphthalidopyruvic acid* crystallises in needles, and melts at 158—159°. The *calcium* and *barium* salts are both crystalline, as are also the corresponding salts of α-naphthalidopyruvic acid.

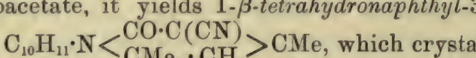
α-Naphthalidopyruvic acid is converted by oxidation with potassium permanganate into its components, which then undergo partial oxidation, free pyruvic acid being also found among the products. α-Dinaphthalidocitric acid undergoes an analogous change when treated in the same way.

*β-Naphthylamine dichloracetate* crystallises in large, colourless plates, melting at 153°. When it is heated with naphthylamine, hydrogen chloride is eliminated, and a yellow, crystalline substance is formed, which has not been obtained pure. When β-naphthylamine is heated with salicylic acid or gallic acid, it is converted into dinaphthylamine. The same change occurs when the base is heated with glyceric acid, but the dinaphthylamine is accompanied by *glyceric β-naphthalide*, which crystallises in plates, and melts at 161—162°. The *benzoyl* derivative melts at 130—131°. A. H.

**Action of Ethylic Cyanoacetate on alc-Tetrahydro-β-naphthylamine.** By A. Benedicenti (*Chem. Centr.*, 1895, ii, 973; from *Ann. Chim. Farm*, **22**, 433—440).—These two compounds react together in the cold, *cyanoacetotetrahydro-β-naphthylamide*,

$$C_{10}H_{11}\cdot NH\cdot CO\cdot CH_2\cdot CN,$$

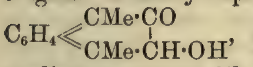
being formed; it crystallises in long, colourless needles, melts at 175—176°, and, when oxidised with potassium permanganate, yields *tetrahydro-β-naphthyloxamic acid*, $C_{10}H_{11}NH\cdot CO\cdot COOH$, which crystallises from water in small crystals, and melts at 163—164°.

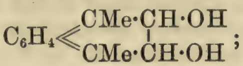
If the amine is first treated with acetone and then with ethylic cyanoacetate, it yields *1-β-tetrahydronaphthyl-3-cyanotrimethylpiperidone*,  $C_{10}H_{11}\cdot N<\begin{matrix}CO\cdot C(CN)\\ CMe_2\cdot CH_2\end{matrix}>CMe$, which crystallises in long needles, melts at 210—211°, and, on oxidation, yields two crystalline compounds, which are being further investigated. In its physiological action, it resembles tetrahydronaphthylamine and not cyanotrimethylpiperidone. J. J. S.

**Dimethylnaphthol obtained from the Santonous acids.** By Stanislao Cannizzaro and Americo Andreocci (*Gazzetta*, 1896, **26**, i, 13—35).—The dimethylnaphthol obtained by the decomposition of the santonous acids (Abstr., 1895, i, 424) has the constitution [$Me_2 : OH = 1 : 4 : 2$], and boils at 315—316° in a current of carbonic anhydride under ordinary pressure. The acetodimethylnaphthylamide derived from it melts at 219—220°, and the dimethylnaphthylamide at 75°; the *hydrochloride* of the latter crystallises in colourless needles, and the *platinochloride* in yellow prisms; the *sulphate* was also prepared. The *formyl* derivative of the amine, obtained by heating it with formic acid, crystallises in needles, melting at 175°; the amine is quantitatively reduced to the original dimethylnaphthol by aqueous nitrous acid, and, on oxidation with alkaline permanganate, yields azodimethylnaphthalene and phthalic acid; the latter acid is also obtained by oxidising the dimethylnaphthol.

1 : 4-*Dimethylnaphthalene* is prepared by the action of sodium

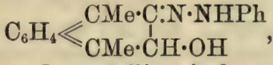
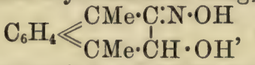
nitrite and stannous chloride on an alcoholic solution of the corresponding dimethylnaphthylamine saturated with hydrogen chloride; it is a colourless liquid heavier than water, and boils at 262·5—263° under 742 mm. pressure. It has the normal vapour density by V. Meyer's method, and yields a *picrate*, $C_{12}H_{12},C_6H_3N_3O_7$, which crystallises in long, yellow needles, melting at 139—141°.

The oxydimethylnaphthol previously described (*loc. cit.*), crystallises in beautiful, anorthic prisms, melting at 104—105°, and may be distilled without decomposition; $a : b : c = 0·8797 : 1 : 0·7877$; $\alpha = 90° 18'$; $\beta = 98° 22'$; $\gamma = 54° 31'$. It is not optically active in solution, and has the normal molecular weight in freezing benzene; on heating with red phosphorus and hydriodic acid, or on warming with stannous chloride and tin in alcoholic solution, it yields the original dimethylnaphthol. It consequently has the constitution  $C_6H_4{<}\begin{array}{l}\text{CMe}\cdot\text{CO}\\ \text{CMe}\cdot\text{CH}\cdot\text{OH}\end{array}$, and, on reduction, probably gives as intermediate product a dihydroxy-compound of the formula



$$C_6H_4{<}\begin{array}{l}\text{CMe}\cdot\text{CH}\cdot\text{OH}\\ \text{CMe}\cdot\text{CH}\cdot\text{OH}\end{array};$$

this, however, could not be isolated.

The *phenylhydrazone*,  $C_6H_4{<}\begin{array}{l}\text{CMe}\cdot\text{C}\colon\text{N}\cdot\text{NHPh}\\ \text{CMe}\cdot\text{CH}\cdot\text{OH}\end{array}$, of oxydimethylnaphthol is readily obtained, and crystallises in long, red needles, melting at 83—84°. The *oxime*,  $C_6H_4{<}\begin{array}{l}\text{CMe}\cdot\text{C}\colon\text{N}\cdot\text{OH}\\ \text{CMe}\cdot\text{CH}\cdot\text{OH}\end{array}$, crystallises in small prisms, melting and decomposing at 175° when rapidly heated; it yields a white, crystalline *acetyl* derivative, $C_{14}H_{15}NO_3$, which melts at 116—117°, and has the normal molecular weight in freezing acetic acid.

2 : 1 : 4-*Nitrosodimethylnaphthalene* is prepared by heating an acetic acid solution of the oxime; it crystallises in long, green needles, melting at 99—100°, is very soluble in organic solvents, and gives the normal molecular weight by the cryoscopic method in benzene solution. It is converted into the 1 : 4 : 2-dimethylnaphthylamine by reduction with zinc dust and acetic acid, and into 2 : 1 : 4-azodimethylnaphthalene by heating with 1 : 4 : 2-dimethylnaphthylamine in alcoholic solution.

*Bisnitrosodimethylnaphthalene*, $C_{24}H_{22}N_2O_2$, is obtained by the action of alcoholic potash on nitrosodimethylnaphthalene; it crystallises in transparent, yellow needles, melting at 174—175°, and is shown to have the molecular composition given above by boiling point determinations in benzene solution. It is accompanied by a small proportion of a *substance* crystallising in yellow laminæ, melting at 205°, and yields an *acetyl* derivative, $C_{24}H_{21}N_2O_2Ac$, in white crystals, melting at 182°. Bisnitrosodimethylnaphthalene is converted into a *substance* of the composition $C_{24}H_{20}N_2O$ by heating with alcoholic potash; it crystallises in white prisms, melting at 180° with preliminary alteration.

W. J. P.

**A new Hydrocarbon, $C_{14}H_{12}$.** By P. SCHICKLER (*J. pr. Chem.*, 1896, [2], **53**, 369—374).—This hydrocarbon is prepared by dropping benzylic ethylic ether into a flask provided with a reflux apparatus, and containing a mixture of benzene with phosphoric anhydride; the mixture is at first kept hot on the water bath, but is cooled when the reaction begins to be violent. Ethylene is evolved, and the liquid assumes a blue fluorescence. After distilling off the benzene and fractionating the residue, a clear, colourless, aromatic liquid is obtained, which can be crystallised by cooling. The new hydrocarbon, $C_{14}H_{12}$, forms thick, hard prisms, the odour of which recalls that of benzylic ethylic ether. It melts at 27—28°, boils at 253—254°, and dissolves in all the usual solvents; solutions of the pure hydrocarbon show no fluorescence. In the absence of benzene, benzylic ethylic ether and phosphoric anhydride react to form a resinous mass of crystalline structure. When other solvents are substituted for benzene, the yield of the hydrocarbon is very poor. Benzylic ether and benzylic alcohol also yield the hydrocarbon when substituted for benzylic ethylic ether in the foregoing prescription.

By nitration, the hydrocarbon yields three nitro-compounds, two of which are crystalline, and appear to be dinitro-compounds, melting at 181° and 108° respectively, whilst the third melts at 75°, but could not be obtained in crystals. Strong sulphuric acid sulphonates and dissolves the hydrocarbon. Beyond these two reactions, the author did not succeed in obtaining any specific compounds from the hydrocarbon, the nature of which, therefore, is not yet elucidated.

A. G. B.

**Extraction of Terpenic Alcohols from Essential Oils.** By ALBIN HALLER (*Compt. rend.*, 1896, **122**, 865—869).—In order to extract the terpenic alcohols which exist in essential oils either in the free state or in the form of ethereal salts, advantage may be taken of the ease with which they combine with the anhydrides of certain dibasic acids, and the tendency of the ethereal salts to decompose. Two methods of treatment are available, but in either case the ethereal salts must first be decomposed by means of alcoholic potash, and the product dried over anhydrous sodium sulphate.

In the first method, the essential oil is heated with the calculated quantity of succinic or phthalic anhydride, either alone or in presence of a hydrocarbon, so that an ethereal hydrogen salt is formed. The product is extracted with a concentrated solution of sodium carbonate, and the alkaline liquid, previously exhausted with ether, is heated on a water bath with excess of sodium hydroxide until no more oil is liberated. Another plan is to acidify the alkaline liquid and separate the ethereal hydrogen salt. In either case, the product is treated with alcoholic potash, and the oil that separates is dried and purified by fractionation.

The second method is applicable to alcohols that would be dehydrated by the acid anhydrides. The dried oil is dissolved in ether or benzene, mixed with a quantity of sodium corresponding with the quantity of alcohol present, and, after removal of any unattacked metal, a quantity of succinic or phthalic anhydride, corresponding with the sodium dissolved, is added. When the action is complete the product is treated with water, and the undissolved oil is washed with a dilute solution of an alkali; the aqueous solutions are washed with ether, and treated as in the first method. Before applying the second method, any aldehydes must be removed, or they will be reduced by the action of the sodium.

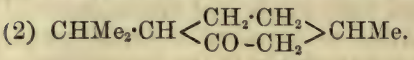
Experiments with several varieties of oil of geranium, oil of peppermint, and oil of spike show that the methods give a good yield of the alcohols present. C. H. B.

**Homolinalol and the Constitution of Licareol and Licarhodol.** By Philippe Barbier and Louis Bouveault (*Compt. rend.*, 1896, **122**, 842—844).—Methylheptenone, when treated with zinc and allylic iodide, yields a tertiary alcohol, as Tiemann and Schmidt have stated. The best yield is obtained if the mixture is allowed to heat spontaneously up to 40—50°. The *methylhexenylallylcarbinol* (*dimethyl*-2 : 6-*octadiene*-2 : 7-*ol*-6) produced is a colourless liquid, which boils at 99—101° under a pressure of 100 mm.; its acetate boils at 110—111° under the same pressure, and yields the original alcohol when hydrolysed.

The authors have repeated the reaction with a number of ketones analogous to methylheptenone, and in all cases have obtained stable tertiary alcohols, which react with acetic anhydride above 150° only, but yield normal acetates from which the original alcohol can be regenerated. In no case is there a conversion into an isomeride analogous to the conversion of licareol into licarhodol. From these results, it would seem that the constitution previously ascribed to licareol is not correct, and having regard to the close connection between licareol and licarhodol on the one hand, and geranaldehyde and methylheptenone on the other, the authors provisionally adopt the constitution $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}C(OH){:}CH_2$ for licareol, and $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH{:}CH{\cdot}OH$ for licarhodol (see Abstr., 1895, i, 77). C. H. B.

**Rhodinaldehyde and its Conversion into Menthone.** By Philippe Barbier and Louis Bouveault (*Compt. rend.*, 1896, **122**, 737—739).—When rhodinol (Abstr., 1895, i, 78) is oxidised with chromic mixture, the product is a mixture of rhodinaldehyde (this vol., i, 446) and menthone. The *semicarbazone* of the former is soluble in ether, melts at 115°, and is not affected by hydrochloric acid, whilst that of the latter is insoluble in ether, and is decomposed by hydrochloric acid. The spontaneous oxidation of oil of pelargonium yields a similar mixture of rhodinaldehyde and menthone, and not a mixture of two ketones as stated in a former paper (Abstr., 1895, i, 4). The same mixture is obtained by the spontaneous oxidation of rhodinol, and the menthone results from an isomeric change in the rhodinaldehyde. If the oxime of a mixture of rhodinaldehyde and menthone is treated with acetic anhydride, it is completely converted into the oxime of menthone. It follows that rhodinaldehyde has the constitution (1) and menthone the constitution (2):

(1) $CMe_2\!:\!CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CHO$.

(2)  $CHMe_2\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CO-CH_2\end{matrix}>CHMe$. C. H. B.

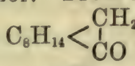
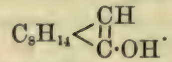
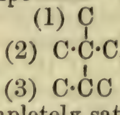
**Citronellaldehyde and its Isomerism with Rhodinaldehyde.** By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 795—796).—Citronellaldehyde (Abstr., 1893, i, 685), obtained from "essence of citronelle, balm-mint of the Indies," forms a *semicarbazone*, which crystallises in micaceous lamellæ, melting at 82°. Citronellic acid is obtained from the nitrile, which is itself prepared from the oxime, and it yields a *paratoluidide* which crystallises from boiling alcohol of 80° in long, slender needles, melting at 95°; whereas the paratoluidide of rhodinic acid melts at 80·5°. Energetic oxidation of citronellaldehyde yields acetone and β-methyladipic acid as well as citronellic acid, and it is, therefore, isomeric with rhodinol, and has the constitution $CMe_2\!:\!CH\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHO$.

C. H. B.

**Essential Oil of Valerian (Valeriana officinalis).** By LOUIS OLIVIÉRO (*Bull. Soc. Chim.*, 1895, [3], **13**, 917—926).—On hydrolysing essential oil of valerian with alcoholic potash, washing the product with water, and after having extracted the wash water with ether, evaporating to a small bulk, acidifying, and distilling, acetic acid, formic acid, and traces of butyric acid are found in the distillate; they probably exist in the essence as bornylic salts.

The ethereal extract yields a lævorotatory, dihydric *alcohol*, $C_{10}H_{20}O_2$, melting at about 132°, $[\alpha]_D = -96°$.

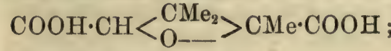
The insoluble portion from the hydrolysis, on fractionation, yields a large quantity of borneol. From the fraction 160—165° a hydrocarbon, $C_{10}H_{16}$, was isolated; it boils at the same temperature as a sesquiterpene, and is lævorotatory $[\alpha]_D = -9° 20'$. J. F. T.

**Structure and Stereochemistry in the Camphor Group.** By OSSIAN ASCHAN (*Chem. Centr.*, 1895, ii, 967—972; from *Acta Soc. Sci. fennice*, **21**, 1—227; compare Abstr., 1894, i, 538 and 615; 1895, i, 154, 188, and 242).—In the first part of the paper, the author discusses the various formulæ, 25 in number, which have been suggested for camphor. From recent researches it follows that (1) camphor is a ketone,  $C_8H_{14}<\begin{matrix}CH_2\\ |\\ CO\end{matrix}$, but can in special cases react in its tautomeric form  $C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot OH\end{matrix}$. (2) Camphoric acid is a dicarboxylic acid, $C_8H_{14}(COOH)_2$. (3) Camphor and camphoric acid are saturated polymethylene compounds. (4) Camphor and camphoric acid contain the grouping  $\begin{matrix}(1) & C\\ & |\\ (2) & C\cdot C\cdot C\\ & |\\ (3) & C\cdot CC\end{matrix}$, in which the carbon atoms 1, 2, and 3 are partially or completely saturated with hydrogen.

From a study of the number of the stereoisomeric camphoric acids (see Abstr., 1894, i, 538), the author concludes that camphoric acid must contain two asymmetric carbon atoms, provided the molecule is unsymmetrical.

The camphoric acids belong to the *cis*-type, and the isocamphoric acids to the *trans*-type.

The properties of the various camphoric acids, anhydrides, brom- and chlor-anhydrides are described in detail. J. J. S.

**Constitution of Camphoric acid.** By LUIGI BALBIANO (*Gazzetta*, 1896, **26**, i, 52—61).—The acid, $C_8H_{12}O_5$, prepared by Mahla and Tiemann (Abstr., 1895, i, 678) and by the author (Abstr., 1894, i, 614; 1895, i, 522) is considered by the German chemists to be a ketonic dicarboxylic acid of the constitution $COOH{\cdot}CHMe{\cdot}CMe_2{\cdot}CO{\cdot}COOH$, and is stated by them to yield a bromophenylhydrazone melting at 161—162°. The author finds that in acetic acid solution the acid, $C_8H_{12}O_5$, reacts readily with parabromophenylhydrazine yielding an additive *compound* of the composition $C_{14}H_{19}BrN_2O_5$; it is a microcrystalline, yellow powder melting with decomposition at 146—147°, and is a dibasic acid. On heating its aqueous solution neutralised with soda, or its alcoholic solution, hydrolysis occurs and a substance $C_{14}H_{17}BrN_2O_4$, is formed, having the composition of a bromophenylhydrazone of the acid, $C_8H_{12}O_5$; this crystallises in microscopic, yellow needles, melting and decomposing at 153—154°, and is a dibasic acid. Its *calcium* salt, $C_{14}H_{15}BrN_2O_4Ca,2H_2O$, is a sparingly soluble, white powder, which loses its water over sulphuric acid, and decomposes at 150°. The acid is not changed by boiling with baryta solution, or by heating in sealed tubes with hydrochloric acid; it is evident that it has not the properties of a hydrazone. The author, therefore, considers that the acid $C_8H_{12}O_5$ is not a ketonic acid, but has the constitution  $COOH{\cdot}CH{<}{\substack{CMe_2\\ O{-}{-}}}{>}CMe{\cdot}COOH$; the additive product might then have the constitution

$$COOH{\cdot}CMe(OH){\cdot}CMe_2{\cdot}CH(COOH){\cdot}N_2H_2{\cdot}C_6H_4Br,$$

and should easily lose water yielding a pyrazolidine derivative.

W. J. P.

**Sandarac Resin.** By A. BALZER (*Arch. Pharm.*, 1896, **234**, 289—316).—Sandarac resin contains a very small amount of an ethereal oil and of a bitter substance, which can be obtained as a yellow powder, but consists chiefly of two acids, sandaracolic acid, the potassium salt of which is insoluble in concentrated potash, and callitrolic acid, the potassium salt of which is soluble. The former constitutes about 85, the latter about 10 per cent. of the crude resin. When submitted to distillation, the resin yields acetic acid, and a substance smelling like camphor.

*Sandaracolic acid*, $OMe{\cdot}C_{43}H_{61}O_3(OH){\cdot}COOH$, is a white, crystalline powder, melting at 140°. The molecular weight was determined by the cryoscopic method in phenol solution. It yields a red solution with sulphuric acid, a sulphonic acid being formed which could not be obtained pure. The *silver salt* of sandaracolic acid has the formula $C_{45}H_{65}AgO_7$, and is a white powder. The *acetyl derivative* and the *benzoyl derivative* are brownish-yellow powders, which could not be obtained crystalline, but yielded satisfactory numbers when analysed. The presence of a methoxy-group in the acid was proved by Zeisel's method. Nitric acid converts the acid into an oxidised product, $C_{40}H_{42}O_{13}$, picric acid being also formed together with oxalic acid, when concentrated nitric acid is used. When distilled with zinc dust, a number of aromatic substances are formed, benzene and toluene having been isolated from the product.

*Callitrolic acid*, $OH\cdot C_{64}H_{82}O_5\cdot COOH$, forms colourless, prismatic crystals melting at 248°, and, like sandaracolic acid, is a monobasic hydroxy-acid. The *copper salt* crystallises from a mixture of alcohol and ether in plates melting at 185°; the *acetyl derivative* is a light brown, amorphous powder.

These two acids afford a further confirmation of the generalisation made by Tschirch (Pringsheims' *Jahrbücher*, 1893, **25**, 379), that all the resin acids of the coniferæ are hydroxy-acids. A. H.

**Luteolin.** By JOSEF HERZIG (*Ber.*, 1896, **29**, 1013—1014; compare A. G. Perkin, Trans., 1896, 206).—Luteolin is not identical with fisetin, $C_{15}H_{10}O_6$, for its acetyl derivative melts at 223—226° (Perkin, 213—215°), whilst acetylfisetin melts at 196—199°. Acetylluteolin gives the same numbers, on analysis, as tetracetylfisetin. The alkyl derivatives of luteolin have not yet been got white, as they should be if they are really tetralkyl derivatives, assuming luteolin to be analogous to fisetin; it is the trialkyl derivatives of fisetin that are yellow. The author thinks that phloroglucinol is really formed in addition to protocatechuic acid when luteolin is decomposed by aqueous alkalis; he recognised it by the pine-splinter test, which is more delicate than the ferric chloride test employed by Perkin. If this is so, luteolin is not closely related to fisetin, but rather to chrysin. [Compare further Perkin, Trans., 1896, 799.]

C. F. B.

**Pharmaceutical and Chemical Characteristics of Cubebs and the Piperaceous Fruits used for its Adulteration.** By KARL PEINEMANN (*Arch. Pharm.*, 1896, **234**, 204—271).—Cubebs, a drug which has been known since the time of the Arabian physicians of the middle ages, was very largely used about 1880 in cases of catarrh, and, in the form of cigarettes, as a remedy for asthma, the result being that it rose very rapidly in price, and was very largely adulterated by the dealers. The various fruits, both piperaceous and belonging to other families, may be, for the most part, distinguished from the true cubebs simply by their external characteristics, whilst others resemble the genuine product so closely that a microscopic examination of a section of the fruit is necessary. A few of the substances employed for this purpose, however, belong to the same species as cubebs, and can only be distinguished by the fact that they do not contain cubebin, and therefore do not give a purple-red coloration with strong sulphuric acid. Cubebin does not occur in the perisperm only, as has hitherto been supposed, but also in the pericarp, and the same is true of the occurrence of piperine in black pepper. Piperaceous plants which contain cubebin or an allied compound do not, as a rule, contain any alkaloïd, such as piperine, but one plant has been found which is an exception to this. *Piper Lowong*, Bl., is found to contain 1·5 per cent. of piperine and 0·71 per cent. of a substance which closely resembles cubebin, but is isomeric with it, and is, therefore, termed *pseudocubebin*, $C_{20}H_{20}O_6$. This compound crystallises in long needles, melts at 122°, and in chloroform solution is dextrorotatory, whilst cubebin melts at 125°, and is lævorotatory. Pseudocubebin, moreover, has no taste, and gives a yellowish-brown coloration with sulphuric acid, whilst cubebin has a penetrating bitter taste, and is coloured a reddish-purple by sulphuric acid. The molecular formula was determined by the boiling point method in benzene solution. By oxidation with potassium permanganate, pseudocubebin is converted into piperonylic acid, in the same way as cubebin, but when fused with potash, it yields no solid product which could be isolated, whilst cubebin is thereby converted into protocatechuic and acetic acids. Bromine converts pseudocubebin into the *dibromo-compound*, which crystallises in silky needles melting at 177°. *Dinitropseudocubebin* crystallises in small, yellow needles, almost insoluble in acetic acid. The corresponding *dinitrocubebin* also forms small needles, melts at 182·5°, and dissolves moderately freely in acetic acid. Pseudocubebin is not attacked by benzoic chloride or sodium ethoxide, and is converted into a brown resin by hydrochloric acid at 100°. Alcoholic hydrogen chloride, on the other hand, converts it into a white, amorphous powder, which could not be obtained pure.

The ethereal oil present in *Piper Lowong*, Bl., may be divided by fractionation into two parts; that which boils at the higher temperature contains a crystalline substance, which melts at 164°, and has the composition $C_{10}H_{20}O_2$.

The substance described as cubebin by various authors does not always appear to be the same compound. The molecular weight of some specimens corresponds with the formula $C_{20}H_{20}O_6$, whilst the molecular formula of others is $C_{40}H_{40}O_{12}$. The melting point, solubility, and even the colour reactions also vary, as do the products obtained by bromination and nitration. A. H.

**Proteacin [Leucodrin].** By OSWALD HESSE (*Annalen*, 1896, **290**, 314—317).—Proteacin is extracted by ether from the leaves of *Leucodendron concinnum*, and is the substance referred to by Beck as protexin, and by Merck as leucodrin; the latter name is now adopted by the author.

*Leucodrin*, $C_{18}H_{20}O_9$, crystallises in colourless, rhombic prisms, and melts at 212°, decomposing at higher temperatures; it is intensely bitter, and dissolves readily in hot water, being more sparingly soluble in cold; the aqueous solution, which is neutral, develops no coloration with ferric chloride. It dissolves in caustic soda, and after treatment with boiling, concentrated sulphuric acid, reduces Fehling's solution. The *triacetyl* derivative crystallises from alcohol.

M. O. F.

**Sugar-bush (Protea Mellifera).** By OSWALD HESSE (*Annalen*, 1896, **290**, 317—321).—*Protea mellifera* is a South African shrub which owes its colloquial name of sugar-bush to the sweet juice extracted from its blossoms; the syrup obtained on evaporating this juice with ginger, finds application as a remedy for catarrh. The shrub has been erroneously regarded as the source of Beck's protexin; the leaves, however, yield a preparation which melts at 172° (compare foregoing abstract), whilst leucodrin melts at 212°. Extraction of the leaves, twigs, and blossoms with ether effects the isolation of two crystalline substances—a phenol and an acid; the former is quinol, whilst the acid stands in the same relation to homoprotocatechuic acid as that substance does to protocatechuic acid.

*Proteaic acid*, $C_6H_2Et(OH)_2 \cdot COOH$, separates from water in white crystals, which become yellow in air; it melts at 187°, carbonic anhydride being eliminated. Whilst indifferent towards Fehling's solution, the acid reduces silver nitrate; solutions of the alkali salts rapidly become dark brown, absorbing oxygen. The *lead* salt, $(C_9H_8O_4Pb)_2,PbO$, is a yellow, crystalline substance, which contains $1H_2O$; it loses water at 120°. M. O. F.

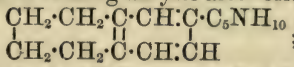
**Chlorophyll. IV.** By EDWARD SCHUNCK and LEO MARCHLEWSKI (*Annalen*, 1896, **290**, 306—313).—A direct comparison of phylloporphyrin (Abstr., 1895, i, 297) with the hæmatoporphyrin of Nencki and Sieber indicates that the relationship between these substances is a close one, and the authors' investigation renders it probable that the latter colouring matter is dihydroxyphylloporphyrin. Nencki and Sieber ascribed to hæmatoporphyrin the formula $C_{16}H_{18}N_2O_3$, whilst phylloporphyrin most probably has the composition $C_{16}H_{18}N_2O$ (compare *loc. cit.*); in chemical properties, moreover, the substances are distinct, phylloporphyrin is insoluble in aqueous alkalis, but yields a crystalline zinc derivative, whilst hæmatoporphyrin dissolves readily in alkalis, but does not give rise to a zinc derivative, and has not been obtained in the crystalline condition. The most striking agreement between the compounds, however, lies in their characteristic absorption spectra, this point being clearly illustrated in the original paper by a plate representing the spectra of the two compounds dissolved in ether and in hydrochloric acid, and of the zinc derivatives in alcoholic solution. M. O. F.

**Action of Halogens on the Colouring Matter of the Kermes Berry (Phytolacca decandra, L.).** By ALBERT HILGER and CARL MAI (*Chem. Centr.*, 1895, ii, 1083—1084; from *Forsch. Ber. Lebensm. Hyg.*, **2**, 343—346).—Chlorine and bromine readily decolorise the juice of kermes berries; iodine, however, has very little action. The authors have prepared a considerable quantity of the decolorised product by adding the juice, previously treated with hydrochloric acid, to a 10 per cent. solution of soda saturated with chlorine. The white, flocculent precipitate (5—6 grams from 8 kilos. of juice), on washing and drying, forms an amorphous, yellowish-grey powder, which is insoluble in water and ether, moderately soluble in aqueous alcohol, sparingly in acetone, chloroform, &c. The solution in potash turns brown after a time, and, on heating, yields chloroform. It is readily converted into acetyl or benzoyl derivatives, and also yields alkyl derivatives; dilute nitric acid dissolves it with evolution of nitrous fumes.

The colouring matter of red grapes and of bilberries is acted on by chlorine and bromine, and also by iodine. J. J. S.

**Pyridineacetone Chloride.** By DANIEL KNUTTEL (*Chem. Centr.*, 1895, ii, 895—896; from *Diss. Marburg*).—The author states that the melting point of the double compound obtained from pyridineacetone chloride and mercuric chloride is 120° (Dreser gives 119°). Copper and cadmium chlorides give no additive compounds. Pyridineacetone chloride, when distilled with soda, is decomposed, and yields pyridine. With hydroxylamine, it yields *pyridineacetoxime chloride*, which melts at 182—184°, its *platinochloride* at 204—205°, and its *aurochloride* at 144—145°; the oxime, when heated with acetic chloride for five hours on the water bath, yields an *acetyl* derivative, the *platinochloride* of which melts at 195° to 197° and the *aurochloride* at 140—141°. Acetic anhydride, benzoic chloride and anhydride, and concentrated hydrochloric acid decompose the oxime. Sodium amalgam and acids, and also formamide, entirely decompose the oxime; moist silver oxide converts the oxime chloride into the free base.

Pyridineacetone chloride, in acetic acid solution, yields, with phenylhydrazine, a *phenylhydrazide*, which melts at 133—134°. Piperidine and chloracetone unite in benzene solution to form a compound already described by Störmer and Burkert; pyridine, apparently, does not unite with chloracetone. J. J. S.

**β-Naphthylpiperidine and β-Naphthyl-2-pipecoline.** By W. ROTH (*Ber.*, 1896, **29**, 1175—1181; compare this vol., i, 253).—β-Naphthylpiperidine, $C_{10}H_7\cdot C_5NH_{10}$ (Lellmann, Abstr., 1890, 1003), was prepared by heating piperidine (1 mol.) with β-naphthol (1 mol.) for four hours at 250—260° in a sealed tube. It melts at 56° (corr.); the *hydrochloride*, *sulphate*, with $3H_2O$, and yellow *aurochloride*, with $4H_2O$, and *picrate* melt respectively at 214°, 105°, 131—132°, and 188°. It is reduced by sodium in boiling amylic alcoholic solution to *tetrahydro-β-naphthylpiperidine*,  $\begin{array}{l} CH_2\cdot CH_2\cdot C\cdot CH{:}C\cdot C_5NH_{10} \\ \,| \qquad\qquad\quad \| \qquad\;\; | \\ CH_2\cdot CH_2\cdot C\cdot CH{:}CH \end{array}$; this is an oil boiling at 274—276° (corr.) under 749 mm., and at 190—196° (corr.) under 24 mm. pressure; its *hydrochloride*, *platinochloride*, with $3H_2O$, *aurochloride*, and *picrate* melt respectively at 210—211°, 156—159°, 135°, and 166°; oxidation with permanganate converts it into adipic and oxalic acids.

*β-Naphthyl-2-pipecoline*, $C_{10}H_{17}\cdot C_5NH_9Me$, was prepared in a similar manner from 2-pipecoline and β-naphthol. It was obtained as a yellowish oil, boiling at 186—190° (corr.) under 10 mm. pressure; the *platinochloride*, with $6H_2O$, and *picrate* melt respectively at 145° and 153—154°; the *hydrochloride* and *aurochloride*, with $9H_2O$, were also prepared and analysed. C. F. B.

**Ladenburg's "Isopipecoline."** By WILHELM MARCKWALD (*Ber.*, 1896, **29**, 1293—1296).—The author maintains his conclusion that "isopipecoline" is a mixture of *d*- and *l*-pipecoline (this vol., i, 253), and shows that Ladenburg's argument (*ibid.*, 378) against it is fallacious. C. F. B.

**4-Nitro-, 1-Nitro-, 4-Amido-, and 1-Amido-quinoline.** By Adolph Claus and Eugen Setzer (*J. pr. Chem.*, 1896, [2], **53**, 390—413).—Details of the best method for nitrating quinoline in order to obtain 1- and 4-nitroquinoline are given. The nitrate of the 4-derivative is so insoluble in nitric acid that it may be separated by this means from the accompanying isomeride. 1-Nitroquinoline forms no additive compound directly with alkylic haloïds. The *methiodide* of 4-nitroquinoline may be prepared by heating its components together; it crystallises in dark red prisms and needles, and melts and decomposes at 215°. 1-Nitroquinoline does not yield a bromo-derivative by the Claus-Collischon method, but 4-nitroquinoline yields 3′-bromo-4-nitroquinoline (m. p. 136°; Abstr., 1889, 728); neither nitroquinoline can be directly brominated.

4-*Nitrocarbostyril* is prepared from 4-nitroquinoline by treating it with a solution of bleaching powder in the presence of boric acid, and decomposing the hypochlorous acid compound which separates by hot aqueous soda; on adding strong hydrochloric acid to the hot alkaline solution, 4-nitrocarbostyril is liberated and separates on cooling. It crystallises from hot alcohol in golden-yellow, lustrous needles and laminæ, and melts at 304°; it is probably identical with the nitrocarbostyril (m. p. 302°) prepared by Claus and Pollitz (Abstr., 1890, 521). No carbostyril could be prepared from 1-nitroquinoline by the bleaching powder reaction (compare Abstr., 1891, 1218; 1888, 502).

2′ : 4-*Chloronitroquinoline* is obtained when 4-nitrocarbostyril is heated with phosphoric chloride; it crystallises in yellowish-green needles, and melts at 130°.

4-*Amidocarbostyril* crystallises in long, silky, colourless needles, melts at 250°, and dissolves in hot water.

By methylating 4-nitrocarbostyril, 4 : 1′-nitromethylquinolone is obtained; it melts at 165°, and is identical with Decker's compound (Abstr., 1892, 880).

1-Amidoquinoline melts at 70° (uncorr.), not 67° as heretofore stated; 4-amidoquinoline melts at 110°, and boils at 310°. By direct bromination, 1-amidoquinoline yields 2 : 4 : 1-dibromamidoquinoline (Abstr., 1894, 553), but bromo-1-amidoquinoline cannot be prepared in this manner; when, however, the acetyl-group is introduced into the amido-group the direct entry of one atom of bromine becomes possible. 1-*Acetamidoquinoline* is best prepared by adding the calculated quantity of acetic anhydride to a solution of 1-amidoquinoline in benzene and evaporating at the ordinary temperature in a current of air; it crystallises from alcohol in colourless, flattened needles, and melts at 103°. 4 : 1-*Bromacetamidoquinoline* crystallises in long, silky, colourless needles, and melts at 140°; its orientation is settled by de-acetylising it, when it yields 4 : 1-bromamidoquinoline (m. p. 104°; Abstr., 1890, 173; 1894, i, 54). The three homonucleal bromo-1-amidoquinolines are now known.

4-Amidoquinoline behaves like the 1-derivative towards bromine, the direct action producing 1 : 3 : 4-dibromamidoquinoline, which has been already described (Abstr., 1895, i, 565). 4-*Acetamidoquinoline* crystallises in lustrous, colourless needles, and melts at 178°; by bromination it yields 4 : 1-acetamidobromoquinoline, which forms yellowish-tinted needles, melts at 250°, and gives rise to 1 : 4-bromamidoquinoline (Abstr., 1893, i, 668) when de-acetylised.

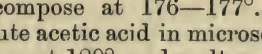
A. G. B.

**Action of Chlorine on Hydroxyquinolines. III. Chlorhydroxy-α-quinolinequinone.** By THEODOR ZINCKE and E. WINZHEIMER (*Annalen*, 1896, **290**, 321—359; compare Abstr., 1891, 1249).—The authors have obtained from 2 : 3-chlorhydroxy-1 : 4-quinolinequinone (*loc. cit.*) a series of derivatives analogous with those obtained by Zincke and Gerland from chlorhydroxy-α-naphthaquinone (Abstr., 1888, 290, 1192, and 1198).

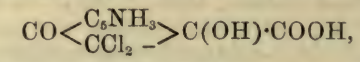
2 : 3-Chlorhydroxy-1 : 4-quinolinequinone is obtained from the product of chlorinating 3-hydroxyquinoline; this substance, tetrachloroketohydroquinoline, is reduced to dichlorohydroxyquinoline, which, on further chlorination, yields tetrachloroketoquinoline, this being converted into anilidotrichloroketoquinoline, and ultimately into monochloranilidoquinolinequinoneanilide, the final stage in the operation consisting in the hydrolysis of the last-named substance. The *sodium* derivative crystallises from water in dark red leaflets; the *acetyl* derivative separates from ether in slender, yellowish needles which melt and decompose at 176—177°. The *aniline* derivative crystallises from dilute acetic acid in microscopic, brick-red needles, which become colourless at 180°, and melt and decompose at 194°; the *oxime* is a yellow, amorphous powder, and dissolves in alkalis.

2 : 1 : 3 : 4-*Chlorotrihydroxyquinoline*, obtained by reducing the quinone with stannous chloride, crystallises in silvery leaflets containing $1H_2O$; it melts at 225°, and in the anhydrous condition is a brick-red powder. The *hydrochloride* crystallises in slender, yellow needles, and melts without undergoing decomposition.

2-*Dichloro*-1 : 3 : 4-*triketohydroquinoline hydrate* is produced when chlorine is passed into a solution of chlorhydroxyquinolinequinone in 10 volumes of glacial acetic acid; it crystallises from a mixture of benzene and acetone in colourless, slender needles or aggregates of prisms, which weather rapidly. The substance melts at about 100°, effervescing vigorously, and yielding chlorhydroxyquinolinequinone; in consequence of this behaviour, the compound has not been obtained in the anhydrous state. The *hydrochloride*, $C_9H_3Cl_2NO_3,HCl + 4H_2O$, is a colourless, crystalline powder, and yields the hydrochloride of chlorhydroxyquinolinequinone when heated at 110°.

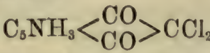
*β-Chloro-α-hydroxypyrindone*,  $C_5NH_3{<}\substack{CO\text{---}\\C(OH)}{>}CCl$, is obtained by treating the foregoing ketone with boiling water, and crystallises from that solvent in long, slender needles or lustrous, red prisms; it becomes dark and chars when heated, but does not melt. The *sodium* derivative crystallises in bright orange leaflets, and the *potassium* derivative forms silky, orange needles; the *anilide* crystallises from alcohol in small, orange needles melting at 162—163°, and dissolves in alkalis.

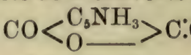
*β-Dichloro-αγ-ketoxypyrhydrindenecarboxylic acid,*



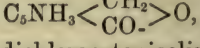
$$CO<\substack{C_5NH_3 \\ CCl_2-}>C(OH)\cdot COOH,$$

is an intermediate compound in the production of the foregoing substance, and is obtained by dissolving dichlorotriketohydroquinoline hydrate or its hydrochloride in 10 per cent. soda, acidifying without delay, and agitating several times with ether; it crystallises from hot, concentrated hydrochloric acid on adding a small quantity of water, and melts at 105—110° with vigorous effervescence. The *methylic* salt separates from ether or benzene in colourless, transparent, monoclinic crystals, and melts and decomposes at 171°.

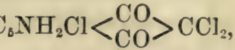
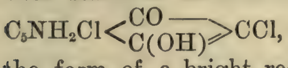
*β-Dichloro-αγ-diketopyrhydrindene,*  $C_5NH_3<\substack{CO \\ CO}>CCl_2$, is obtained by passing chlorine into concentrated hydrochloric and glacial acetic acids containing chlorhydroxypyrindone in suspension; the *hydrochloride* separates from this liquid in transparent prisms, and yields the diketone on treatment with water. The substance is readily soluble, and crystallises from dilute alcohol in white needles melting at 106—107°; the *platinochloride* forms golden-yellow prisms, and melts at 200°.

*β-Dichloracetopicolinic acid,* $COOH\cdot C_5NH_3\cdot CO\cdot CHCl_2$, is prepared by suspending the hydrochloride of dichlorodiketopyrhydrindene in water, and slowly adding the liquid to excess of caustic soda; the product is obtained on acidifying the liquid, and crystallises from glacial acetic acid in lustrous, brownish prisms, which melt and effervesce at 151°. Hot, fuming sulphuric acid converts it into the *lactone* of *β-dichloroxyvinylpicolinic acid,*  $CO<\substack{C_5NH_3 \\ O\text{———}}>C{:}CCl_2$, which crystallises from alcohol in long, slender, white needles, and melts at 135—136°.

*β-Trichloracetopicolinic acid,* $CCl_3\cdot CO\cdot C_5NH_3\cdot COOH$, is obtained on chlorinating dichloracetopicolinic acid dissolved in sodium carbonate, and by the action of bleaching powder on chlorhydroxyquinolinequinone or the triketo-compound; it crystallises from hot, dilute hydrochloric acid in colourless, lustrous leaflets, and melts and decomposes at 174°. Caustic soda resolves the substance into chloroform and quinolinic acid.

The *lactone* of *β-hydroxymethylpicolinic acid,*  $C_5NH_3<\substack{CH_2 \\ CO-}>O$, is produced on heating the foregoing lactone or dichloracetopicolinic acid in sealed tubes with concentrated hydrochloric acid for three hours at 165°, carbonic anhydride being eliminated; it crystallises from methylic alcohol in long, colourless, lustrous needles having the appearance of leaflets, and melts at 161°. The *platinochloride* crystallises in lustrous, golden-yellow prisms, and contains $2H_2O$; barium hydroxide converts the lactone into the *barium* salt, which crystallises from water in brownish prisms containing $2H_2O$.

*β-Methylpicolinic acid,* $C_5NH_3Me\cdot COOH$ [Me : COOH = 3 : 2], is obtained by reducing the foregoing lactone with hydriodic acid, and crystallises from alcohol in nodules of yellowish prisms, which melt at 111°. The *hydrochloride* forms lustrous, white leaflets, and the *platinochloride* crystallises from absolute alcohol in small, yellow prisms, and melts at 192°; the crystals contain $2H_2O$, which is lost at 100°.

*β-Dichloro-αγ-diketochloropyrhydrindone*,  $C_5NH_2Cl<\substack{CO\\CO}>CCl_2$, arises from chlorohydroxypyrindone by chlorination in absence of hydrochloric acid; it crystallises from glacial acetic acid on adding a small quantity of water to the solution, and melts at 100°. Reduction with stannous chloride converts it into *chlorhydroxychloropyrindone*,  $C_5NH_2Cl<\substack{CO\text{—}\\C(OH)}\geqslant CCl$, which separates from glacial acetic acid in the form of a bright red, crystalline powder; it darkens at 150°, sinters at 170°, melts and decomposes at 180°.

*Dichloracetochloropyridinecarboxylic acid*,

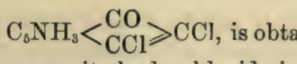
$$CHCl_2{\cdot}CO{\cdot}C_5NH_2Cl{\cdot}COOH,$$

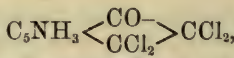
is obtained by the action of soda on the foregoing diketo-compound; it crystallises from benzene in colourless, microscopic needles, and melts to a red liquid at 148°. M. O. F.

**Action of Chlorine on Hydroxyquinolines. IV. Dichloro-β-quinolinequinone.** By THEODOR ZINCKE and K. WIEDERHOLD (*Annalen*, 1896, **290**, 359—382; compare the foregoing abstract).—1 : 2-*Dichloro*-3 : 4-*quinolinequinone* (*dichloro-β-quinolinequinone*) is readily obtained by the action of chlorine on 3 : 4-hydroxyamidoquinoline in glacial acetic acid, and crystallises from alcohol in lustrous, yellow leaflets melting at 180°. The *hydrochloride* is a bright yellow, crystalline powder containing $1H_2O$; it melts and decomposes at 199—200°.

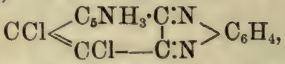
1 : 2 : 3 : 4-*Dichlorodihydroxyquinoline* (*dichloro-β-quinolinequinol*) is obtained by reducing the quinone in alcoholic solution with stannous chloride; it is a red powder which begins to sublime and decompose at 150°. The *hydrochloride* crystallises in slender, yellow needles containing $1H_2O$, and melts and decomposes at 170°.

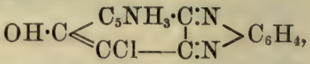
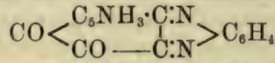
Aniline converts dichloro-β-quinolinequinone into 2 : 3-chlorhydroxy-4 : 1-quinolinequinoneanilide, already described by Zincke and Müller (Abstr., 1891, 1251); this melts at 175°, and not at 195°. The *paratoluidide* crystallises from alcohol or benzene in long, dark red needles, and melts at 178—180°; hydrolysis converts it and the anilide into chlorhydroxy-α-quinolinequinone (foregoing abstract).

*αβ-Dichloropyrindone*,  $C_5NH_3<\substack{CO\\CCl}\geqslant CCl$, is obtained by suspending dichloro-β-quinolinequinone or its hydrochloride in water, and adding the liquid to ice-cold caustic soda solution containing sodium peroxide; it crystallises from methylic alcohol in long, slender, lustrous needles, and melts at 112°. It volatilises at higher temperatures, and is also volatile in an atmosphere of steam. Aniline converts it into α-anilido-β-chloropyrindone (m. p. 162—163°), described in the foregoing abstract.

*Tetrachloropyrhydrindone*,  $C_5NH_3<\begin{array}{l}CO-\\CCl_2\end{array}>CCl_2$, is produced by chlorinating $\alpha\beta$-dichloropyrindone in chloroform. Caustic soda converts it into *trichlorovinylpyridinecarboxylic acid*, $CCl_2{:}CCl{\cdot}C_5NH_3{\cdot}COOH$, which crystallises from benzene in greyish needles, and melts at 153—154°.

*Dichlorovinylpyridinecarboxylic acid*, $CHCl{\cdot}CCl{\cdot}C_5NH_3{\cdot}COOH$, is obtained by the action of dilute soda on $\alpha\beta$-dichloropyrindone; it crystallises from benzene in needles, and melts at 139°.

1 : 2-*Dichloroquinolinephenazine*,  $CCl<\begin{array}{l}C_5NH_3{\cdot}C{:}N\\CCl\text{——}C{:}N\end{array}>C_6H_4$, is obtained on adding orthophenylenediamine dissolved in glacial acetic acid to a solution of dichloro-$\beta$-quinolinequinone in methylic alcohol; it crystallises from alcohol, and melts at 239—240°.

2 : 1-*Chlorhydroxyquinolinephenazine*,  $OH{\cdot}C<\begin{array}{l}C_5NH_3{\cdot}C{:}N\\CCl\text{——}C{:}N\end{array}>C_6H_4$, arises from treatment of chlorhydroxy-$\alpha$-quinolinequinone with orthophenylenediamine; it crystallises in lustrous, yellow needles, and melts above 200°. The *hydrochloride* is a carmine substance, and the *sodium* derivative is sparingly soluble in water. On suspending the eurhodole in glacial acetic acid, and adding a few drops of concentrated nitric acid to the hot liquid, 1 : 2-*diketoquinolinephenazine hydrate*,  $CO<\begin{array}{l}C_5NH_3{\cdot}C{:}N\\CO\text{——}C{:}N\end{array}>C_6H_4,H_2O$, is produced; it separates from glacial acetic acid as a yellow, crystalline powder, and melts above 270°. Orthophenylenediamine converts it into a yellowish-white compound which crystallises from alcohol in leaflets; this is probably a diphenazine derivative. M. O. F.

**Iodisoquinoline; the two isomeric Iodophthalic acids.** By Albert Edinger (*J. pr. Chem.*, 1896, [2], **53**, 375—389; compare Abstr., 1895, i, 300).—*α-Iodisoquinoline* is prepared by diazotising α-amido-isoquinoline and immediately dropping the diazotised solution into a concentrated solution of potassium iodide; after 12 hours the solution is made strongly alkaline and distilled in steam. It sublimes at 100° in lustrous, white needles, melts at 98°, and is freely soluble in alcohol, ether, acetone, benzene, chloroform, &c., but only sparingly in hot water; it is a strong, tertiary base; the *methiodide* is anhydrous, and melts at 306°; the *platinochloride* decomposes at 298°; the *picrate* is anhydrous, and melts at 224°; the *dichromate* is described.

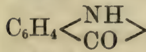
*α-Iodophthalimide* is obtained by oxidising a neutral solution of α-iodisoquinoline sulphate with potassium permanganate. It crystallises from hot water in white needles, melts at 238°, and may be sublimed. For the identification of this compound, it was prepared synthetically from phthalic anhydride, this being first converted into ethylic hydrogen α-nitrophthalate by Miller's method (Abstr., 1882, 404). The author notes that ethylic hydrogen α-nitrophthalate crystallises with $2\frac{1}{2}H_2O$, and melts in this water at 50°, the anhydrous compound melting at 110°. Ethylic β-nitrophthalate melts at 34°.

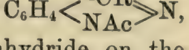
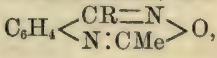
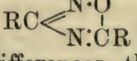
α-Nitrophthalic acid was diazotised and converted into the iodo-acid by Bernthsen's method (Abstr., 1886, 363). The α-iodophthalic anhydride prepared in this way melted at 153°, and when heated in ammonia, yielded an imide which melted at 238°. α-Iodophthalic acid crystallises with $3H_2O$, and melts at 206°. The same acid, anhydride and imide, were prepared from diethylic α-iodophthalate (m. p. 70°). *Potassium α-iodophthalate*, with $3H_2O$, and the *barium*, *silver*, and *copper*, with $2\frac{1}{2}H_2O$, salts are described.

β-Iodophthalic acid was prepared by reducing and diazotising (in hydriodic acid solution) the normal β-ethylic salt obtained by Miller's method (*loc. cit.*), and hydrolysing the product. It was found to crystallise with $1\frac{1}{2}H_2O$, and to melt at 182°. The imide melts at 222—224°, and the anhydride at 123°. The acid was also prepared by oxidising barium β-iodo-1′- and β-iodo-4′-naphthalenesulphonate with potassium permanganate. The *normal copper*, with $3H_2O$, *silver*, *potassium*, and *barium* salts are described.

The α- and β-acids may be separated by means of their barium salts, that of the α-acid being the more soluble. The α-acid yields the ethylic hydrogen salt when treated with alcoholic hydrogen chloride; whilst the β-acid yields the normal ethylic salt; compare the behaviour of the nitro-acids (Miller's method, *loc. cit.*).

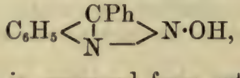
A. G. B.

**A remarkable Formation of Acridone.** By AMÉ PICTET and A. HUBERT (*Ber.*, 1896, **29**, 1189—1191).—When salicylanilide, $C_6H_5\cdot NH\cdot CO\cdot C_6H_4\cdot OH$, is distilled, the main product, which remains in the carbonaceous residue, is not phenanthridone, but acridone,  $C_6H_4{<}\begin{matrix}NH\\CO\end{matrix}{>}C_6H_4$ (compare Abstr., 1892, 1086). The anilide must have first undergone a molecular transformation into phenylanthranilic acid, $COOH\cdot C_6H_4\cdot NH\cdot C_6H_5$, and it is evidence in favour of this that diphenylamine was found in the distillate. Salicyl-2-toluidide and 4-toluide behave in a similar manner, yielding 2-methylacridone and 4-methylacridone respectively (Abstr., 1894, i, 530). C. F. B.

**Indazole Derivatives.** By KARL AUWERS (*Ber.*, 1896, **29**, 1255—1271).—The preparation of indazole derivatives,  $C_6H_4{<}\begin{matrix}-CR\\NAc\end{matrix}{\geqslant}N$, by the action of glacial acetic acid and acetic anhydride on the oximes of aromatic orthoamidoketones has been described by Auwers and Meyenburg (Abstr., 1891, 1375). Bischler has suggested (Abstr., 1893, i, 609) that the acetyl group participates in the reaction, and that the compounds are isindazole derivatives,  $C_6H_4{<}\begin{matrix}CR{=}N\\N{:}CMe\end{matrix}{>}O$, analogous to Tiemann's azoximes,  $RC{<}\begin{matrix}N\cdot O\\ N{:}\overset{|}{C}R\end{matrix}$; in general properties, the compounds exhibit marked differences, the former are volatile with steam, unstable towards alkali, and are strongly basic; whilst the latter are neutral, extremely readily volatile, and very stable towards both alkalis and acids.

With A. R. Ewing.—1′-*Acetylisindazole*, $C_6H_4<{\overset{-CH}{\underset{NAc}{}}}>N$, prepared from orthamidobenzaldoxime, crystallises in slender, almost colourless needles, with an indazole-like smell, gives a crystalline salt with mercuric chloride, and regenerates the oxime when treated with alkali at the ordinary temperature. The melting point of acetylorthamidobenzophenone was previously stated to be 72°, although Bischler and Barad (*loc. cit.*) state that it melts at 88·5—89°; a substance melting at this temperature was obtained in small quantity; further purification failed to change the melting point of the chief product, but subsequent preparations all melted at 88—89°. 1′ : 3′-Acetylphenylisindazole melts at 185°, and has been previously described; the *acetate* crystallises in prisms, and is quickly dissociated when boiled with water. By the action of highly dilute alcoholic soda on the isindazole, *orthacetamidobenzophenoneoxime*, $NHAc{\cdot}C_6H_4{\cdot}CPh{:}N{\cdot}OH$, is formed; it crystallises in lustrous plates, melts at about 180°, and yields a diacetyl derivative. When further treated with soda, both the isindazole and the monacetyloxime yield an orthamidobenzophenone oxime melting at 125—126° (the melting point was previously stated to be 123—125°); it is stereoisomeric with the ordinary compound (m. p. 156°) into which both it and the isindazole are converted by prolonged boiling with soda; the reverse change occurs if the oxime of higher melting point is heated with absolute alcohol during several hours at 160—170°.

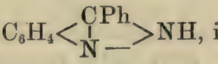
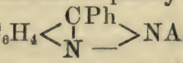
With A. Sondheimer.—2′ : 3′-*Hydroxyphenylindazole*,



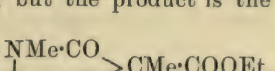
$$C_6H_5<{\overset{CPh}{\underset{N}{|}}}\!\!\!\!\!\!\!\!\!\!\!\!\!\quad\overline{\phantom{xx}}>N{\cdot}OH,$$

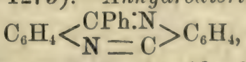
first noticed by Ewing, is prepared from orthamidobenzophenone by means of the diazo-reaction; it crystallises from water in slender, colourless, lustrous plates; from benzene in highly lustrous, pale yellow prisms, and melts at 125—126°. The purified compound is stable, but the presence of foreign matter causes rapid decomposition, especially on exposure to light. When boiled with water, benzophenone is produced in small quantity; distillation under reduced pressure also regenerates benzophenone, and nitrogen is evolved. Under conditions fully described in the original paper, the yield of indazole is 70 per cent. of the theoretical. The *mercurichloride* and *silver nitrate* crystallise from water in colourless needles. Hydrogen chloride in ethereal solution, benzoic chloride, picric acid, acetic anhydride, and phenylic cyanate are without action on the indazole, whilst acetic chloride decomposes it completely; it is oxidised by Fehling's solution, yielding a yellowish-red oil.

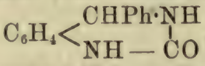
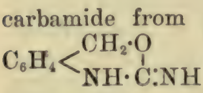
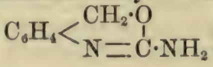
*Isohydroxyphenylindazole*, $C_{13}H_{10}N_2O$, is formed together with benzophenone (10 per cent.) by the action of dilute soda on the hydroxy-derivative; it crystallises in pearly, lustrous plates or needles melting at 212°. It is soluble in alkalis and in concentrated acids, and is reprecipitated from the latter on dilution; it may be crystallised from dilute hydrochloric acid. Attempts to reduce it have been unsuccessful. The yield is 50 per cent. of the theoretical; the molecular weight was determined by means of the cryoscopic method. The *acetyl* derivative crystallises in long, colourless needles melting at 90—91°.

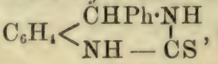
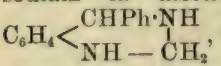
3'-*Phenylindazole*,  $\mathrm{C_6H_4}<\substack{\mathrm{CPh} \\ | \\ \mathrm{N}\text{—}}>\mathrm{NH}$, is formed in small quantity, along with the hydroxyphenylindazole, or by the reduction of the latter with zinc dust in alkaline or acid solution, but the best results are obtained by the use of stannous chloride; it crystallises in long, lustrous needles, melts at 107—108°, resolidifies at 109—110°, and melts again at 115—116°; the form having the higher melting point crystallises from light petroleum in highly lustrous prisms, and is reconverted into the first modification by heating above its melting point. From solution, either form is deposited by the introduction of a crystal of the desired modification. The compound crystallises from soda in needles; when distilled under the ordinary pressure benzaldehyde is formed in traces. The yield is 85—90 per cent. of the theoretical. The *mercuric* and *silver* derivatives crystallise in needles; the *sulphate* is deposited in silky, lustrous needles; the *hydrochloride*, $C_{13}H_{10}N_2,HCl$, is crystalline and pulverulent; both salts are decomposed by water or soda, the modification of the indazole of lower melting point being regenerated. The *picrate* crystallises in dark yellow. lustrous rhomboids which effloresce on exposure to air. The *nitroso*-derivative is yellow, unstable in air, and difficult to purify; it softens at 70—80°. 2' : 3'-*Acetylphenylindazole*,  $\mathrm{C_6H_4}<\substack{\mathrm{CPh} \\ | \\ \mathrm{N}\text{—}}>\mathrm{NAc}$, prepared by the action of acetic anhydride on either modification of phenylindazole, crystallises in needles melting at 69—70°; with alkali, the modification of phenylindazole having lower melting point is regenerated. The constitution of these indazole derivatives cannot be regarded as definitely proved, and the subject is being further investigated. J. B. T.

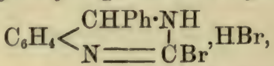
**The Pyrazolone Series.** By SIEGFRIED RUHEMANN (*Ber.*, 1896, **29**, 1016—1018).—Methylchloroform does not react with ethylic sodiomalonate, as chloroform itself does, to form ethylic dicarboxyglutaconate. Ethylic trichloracetate reacts, but the product is the same as when chloroform is employed.

1 : 4-Dimethylpyrazolone-4-carboxylic acid,  $\substack{\mathrm{NMe{\cdot}CO} \\ | \\ \mathrm{N=CH}}>\mathrm{CMe{\cdot}COOEt}$, like the 1 : 4-phenylmethyl acid, is much more stable than the unsubstituted acid; it loses carbonic anhydride, however, at its melting point, 222°. C. F. B.

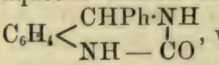
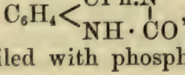
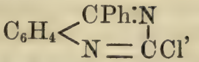
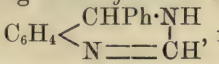
**A Compound containing a Ring of Eight Atoms.** By A. SONDHEIMER (*Ber.*, 1896, **29**, 1272—1275).—*Anhydrodiorthamidobenzophenone* or *diphenylphenhomazine*,  $\mathrm{C_6H_4}<\substack{\mathrm{CPh{:}N} \\ \mathrm{N=C}}>\mathrm{C_6H_4}$, is prepared by heating orthamidobenzophenone hydrochloride between watch glasses at about 130°; the product is dissolved in ether, and the ketone separated by means of hydrochloric acid; it is deposited from light petroleum in yellow crystals, from glacial acetic acid and alcohol in fatty, lustrous plates, and melts at 190°, subliming at higher temperatures. It is stable towards alkalis, dilute acids, and reducing agents; when heated with concentrated sulphuric acid at 160°, orthamidobenzophenone is quantitatively regenerated. Cryoscopic molecular weight determinations agree with the above formula. The yield of the azine is 30 per cent. of the theoretical, and some benzeldehyde is also formed; by friction, the azine becomes highly alectrified, so that it is powdered with difficulty, the best way being to mix it with finely divided glass. J. B. T.

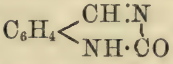
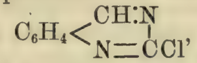
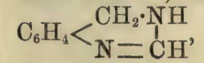
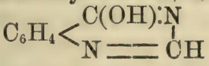
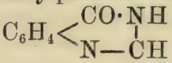
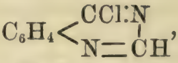
**Quinazoline Compounds.** By SIEGMUND GABRIEL and ROBERT STELZNER (*Ber.*, 1896, **29**, 1300—1316).—Orthamidobenzhydrol, $NH_2\cdot C_6H_4\cdot CHPh\cdot OH$, does not react quite in the same way as orthamidobenzylic alcohol, $NH_2\cdot C_6H_4\cdot CH_2\cdot OH$ (Abstr., 1895, i, 190, 432). Unlike the latter, it yields a crystallised thiotetrahydroquinazoline with thiocyanic acid, whilst it does not yield a carbamide with cyanic acid; it forms the anhydride of such a carbamide, however, when heated with carbamide itself, but this anhydride has the constitution  $C_6H_4<\begin{matrix}CHPh\cdot NH\\ NH - CO\end{matrix}$, whereas the anhydride of the carbamide from orthamidobenzylic alcohol has the constitution  $C_6H_4<\begin{matrix}CH_2\cdot O\\ NH\cdot C{:}NH\end{matrix}$ or  $C_6H_4<\begin{matrix}CH_2\cdot O\\ N = C\cdot NH_2\end{matrix}$ (Paal and Vanvolxem, Abstr., 1894, i, 621).

*Orthamidobenzhydrol* was prepared by reducing orthamidobenzophenone with sodium amalgam in warm, aqueous alcoholic solution; it melts at 120°, its *acetyl derivative* at 118°. When warmed with dilute thiocyanic acid or a mixture of normal potassium thiocyanate solution with hydrochloric acid, it yields 4′-*phenylthiotetrahydroquinazoline*,  $C_6H_4<\begin{matrix}CHPh\cdot NH\\ NH - CS\end{matrix}$, melting at 230°. This can be reduced by sodium in alcoholic solution to 4′-*phenyltetrahydroquinazoline*,  $C_6H_4<\begin{matrix}CHPh\cdot NH\\ NH - CH_2\end{matrix}$, the *hydrochloride* of which begins to decompose at about 200°. When suspended in acetic acid and brominated, it yields 2′ : 4′-*bromophenyldihydroquinazoline hydrobromide*,



$$C_6H_4<\begin{matrix}CHPh\cdot NH\\ N = CBr\end{matrix},HBr,$$

which turns brown at 200°, and melts and decomposes at 273—274°; the bromo-base itself melts at 165°, and, when boiled with excess of aqueous sodium carbonate, yields 4′-*phenyltetrahydro*-2′-*quinazolone*,  $C_6H_4<\begin{matrix}CHPh\cdot NH\\ NH - CO\end{matrix}$, which melts at 193° (the *acetate* at 132—133°), and is also formed when orthamidobenzhydrol is heated with carbamide at 175°. If orthamidobenzophenone is heated with carbamide at 195°, yellow 4′-*phenylquinazolone* (4′-phenyl-2′-ketodihydroquinazoline),  $C_6H_4<\begin{matrix}CPh{:}N\\ NH\cdot CO\end{matrix}$, melting at 250—251°, is formed. This, when boiled with phosphoric oxychloride and pentachloride, yields yellow 2'-*chloro-4'-phenylquinazoline*,  $C_6H_4<\begin{array}{l}CPh{:}N\\ N=CCl\end{array}$, which melts at 113°, and is reduced by boiling with hydriodic acid and phosphorus to 4'-*phenyldihydroquinazoline*,  $C_6H_4<\begin{array}{l}CHPh{\cdot}NH\\ N=CH\end{array}$, melting at 165—166°. The latter is also obtained by reducing the above mentioned bromo-base with hydriodic acid and phosphorus at 180—190°; its *hydrochloride*, orange *platinochloride*, yellow *aurochloride*, yellow *picrate*, and yellow *nitroso-derivative* melt at 242—243°, 234°, 181—182°, 213—214°, and 131° respectively.

Quinazolone (2'-ketodihydroquinazoline),  $C_6H_4<\begin{array}{l}CH{:}N\\ NH{\cdot}CO\end{array}$ (Abstr., 1895, i, 433), when boiled with phosphorus pentachloride and oxychloride, yields yellowish 2'-*chloroquinazoline*,  $C_6H_4<\begin{array}{l}CH{:}N\\ N=CCl\end{array}$, which melts at 108°; this is reduced by hydriodic acid to dihydroquinazoline,  $C_6H_4<\begin{array}{l}CH_2{\cdot}NH\\ N=CH\end{array}$, melting at 126—127°. With phosphorus pentachloride and oxychloride, 4'-hydroxyquinazoline (4'-ketodihydroquinazoline),  $C_6H_4<\begin{array}{l}C(OH){:}N\\ N=CH\end{array}$ or  $C_6H_4<\begin{array}{l}CO{\cdot}NH\\ N-CH\end{array}$ (von Niementowski, Abstr., 1895, i, 571) yields 4'-chloroquinazoline,  $C_6H_4<\begin{array}{l}CCl{:}N\\ N=CH\end{array}$, which melts at 96°, and has a great tendency to go back into the hydroxy-compound.

Orthocyanodiphenylmethane, $CN{\cdot}C_6H_4{\cdot}CH_2Ph$ (Cassirerer, Abstr., 1893, i, 16) can be converted by chlorination at 150—160° into *α-chlororthocyanodiphenylmethane*, $CN{\cdot}C_6H_4{\cdot}CHPhCl$. This is an oil, which, when heated with hydrochloric acid at 150°, yields phthalimide, and, when boiled with aqueous-alcoholic potassium cyanide, does not yield dicyanodiphenylmethane, but *cyanohydroxydiphenylmethane*, $CN{\cdot}C_6H_4{\cdot}CHPh{\cdot}OH$, which is also an oil. C. F. B.

**Orthamidobenzylamines. III.** By MAX BUSCH [and KARL DIETZ] (*J. pr. Chem.*, 1896, [2], **53**, 414—427; compare Abstr., 1894, i, 146; 1895, i, 306, 307).—Formaldehyde condenses with orthamidobenzylamine to form tetrahydroquinazoline; with orthamidobenzylaniline to form 3'-phenyltetrahydroquinazoline; with orthamidobenzylparatoluidine to form 3'-*paratolyltetrahydroquinazoline* (long, white needles, m. p. 127°); with orthamidobenzylorthotoluidine to form 3'-*orthotolyltetrahydroquinazoline* (white crystals, m. p. 140°); with orthamidobenzylorthanisidine to form 3'-*orthanisyltetrahydroquinazoline*, which forms colourless crystals, melts at 141—142°, and dissolves in light petroleum, benzene, and chloroform, but less readily in ether or alcohol. These condensation products are decomposed into their parent compounds by acids.

Orthamidobenzylamine condenses with metanitrobenzaldehyde to form 2'-*metanitrophenyltetrahydroquinazoline*, which crystallises in pale yellow, transparent prisms, melts at 84—85°, and dissolves freely in the usual organic solvents; dilute mineral acids decompose it into the base and aldehyde. With orthonitrobenzaldehyde, orthamidobenzylamine condenses to form a *compound*, probably

$$NO_2\cdot C_6H_4\cdot CH\colon N\cdot C_6H_4\cdot CH_2\cdot N\colon CH\cdot C_6H_4\cdot NO_2\ [= 1:2;\ 1:2;\ 1:2],$$

which crystallises in lustrous, yellow prisms, softens at 125°, and melts at 128°: it is freely soluble in benzene and chloroform, sparingly in ether and alcohol, and almost insoluble in light petroleum.

2'-*Parahydroxyphenyltetrahydroquinazoline* is the product of the condensation of parahydroxybenzaldehyde with orthamidobenzylamine; it crystallises from dilute alcohol in thick, nearly colourless needles, melts at 167—168°, and is scarcely at all soluble in light petroleum, sparingly in benzene, chloroform, and hot water, freely in alcohol.

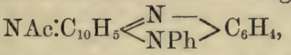
The *compound* $OH\cdot C_6H_4\cdot CH\colon N\cdot C_6H_4\cdot CH_2\cdot N\colon C_6H_4\cdot OH$ is formed from orthamidobenzylamine and salicylaldehyde; it crystallises in transparent yellow prisms and silky needles, melts at 107—108°, and dissolves freely in alcohol and benzene, sparingly in ether and light petroleum.

Orthamidobenzylphenylhydrazine and formaldehyde condense to form a dimethylene *compound*, $CH_2\colon N\cdot C_6H_4\cdot CH_2\cdot NPh\cdot N\colon CH_2$, which crystallises in reddish prisms and needles, melts at 84°, and dissolves freely in benzene, less freely in alcohol and ether, and sparingly in light petroleum; with dilute sulphuric acid it gives formaldehyde.

A. G. B.

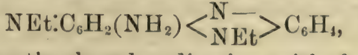
**Relationship of Indulines to Safranines.** By FRIEDRICH KEHRMANN (*Annalen*, 1896, **290**, 247—306; compare Abstr., 1895, i, 148 and 527, also Fischer and Hepp, Abstr., 1895, i, 608, and this vol., i, 50).—The author's experiments lead him to the conclusion that the indulines and safranines represent the amido- and hydroxy-derivatives of one large group of azonium bases; those bases which are not substituted exist in the form of hydrates, in this respect resembling those derivatives which, by reason of the position of the substituents, have not the property of forming paraquinonoïd anhydrides (indulines or indones). The substituted azonium bases, on the other hand, which have the amido- or hydroxy-group in a favourable position, although sometimes occurring as hydrates, exhibit a tendency to lose water, as in the case of rosinduline, aposafranine, and phenosafranine. The indulines and indones arising in this manner, however, yield salts identical with those of the respective azonium hydrates, molecular rearrangement to the orthoquinonoïd azonium type occurring simultaneously with salt formation (compare Abstr., 1895, i, 527).

With M. HERTZ.—When acetamidonaphthaquinone and phenylorthophenylenediamine hydrochloride are heated together in alcohol, condensation takes place, and two isomeric hydrochlorides are produced (Abstr., 1895, i, 148); these may be separated by fractional crystallisation, or by the application of ammonium carbonate. The less soluble hydrochloride, $C_{24}H_{17}N_3O,HCl$, crystallises from alcohol or hot water in red needles with green iridescence, the alcoholic solution being yellowish-red, and exhibiting greenish-yellow fluorescence. This modification decomposes at 290°, whilst 260° is the point at which the more soluble hydrochloride decomposes; the latter crystallises from alcohol in dark, brownish-red plates having a blue lustre, and the solution, which is dark red, does not exhibit fluorescence. The former modification yields rosinduline hydrochloride on elimination of the acetyl group, the same change in the more soluble modification giving rise to an isomeric rosinduline hydrochloride. Both forms of the original salt yield a bright red, crystalline *platinochloride*, and the *hydrogen sulphate* of the more soluble modification crystallises in brownish-red, lustrous needles; the behaviour of the isomerides towards various agents is described in the original paper.

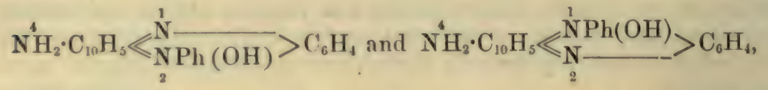
*Acetylrosinduline*,  $NAc{:}C_{10}H_5<\begin{smallmatrix}N—\\NPh\end{smallmatrix}>C_6H_4$, is obtained by adding aqueous alkali or alkali carbonates to a solution of the less soluble hydrochloride, and crystallises from a mixture of alcohol and benzene in small, dark red plates with golden lustre; it is also formed when rosinduline hydrochloride is heated with sodium acetate and acetic anhydride.

*Rosinduline hydrate* is produced by adding ammonia in slight excess to a cold dilute solution of the hydrochloride, and treating the liquid with a few drops of ether, in order to induce crystallisation; it is important that the ammonia employed should be free from carbonate, as, in presence of moisture, the base absorbs carbonic anhydride with great readiness. At 100—110° the hydrate loses $1H_2O$, and is converted into the anhydrous form of rosinduline, described already by Fischer and Hepp; the hydrate melts at 185—187°, the anhydride at 195°, and, whilst the latter dissolves readily in ether and benzene, the hydrate is sparingly soluble in them.

*Rosinduline carbonate*, $(C_{22}H_{16}N_3)_2CO_3$, is obtained in short, dark red, prismatic crystals, containing $4H_2O$; it is sparingly soluble in cold water, but dissolves readily at 40—50°, and, on boiling the solution, carbonic anhydride is evolved, and the anhydrous base crystallises from the almost colourless liquid.

The property of forming carbonates is exhibited by many other feeble azonium bases, and the author describes experiments with the oxidation products of alkylated orthodiamines, which Fischer and Heiler (Abstr., 1893, i, 266) regard as induline derivatives. Thus, the oxidation product of phenylorthophenylenediamine, which is isomeric with anilineaposafranine (Abstr., 1895, i, 528), absorbs no trace of carbonic anhydride in the crystalline condition or in aqueous solution, but, on saturating the ethereal solution with water and leading a stream of carbonic anhydride through the liquid, the carbonate separates in dark brown crystals with green lustre; on boiling an aqueous solution, the same phenomena are observed as in the case of rosinduline carbonate. A further illustration is afforded by the *compound*,  $NEt{:}C_6H_2(NH_2)<\begin{smallmatrix}N—\\NEt\end{smallmatrix}>C_6H_4$, obtained by the oxidation of ethylorthophenylenediamine with ferric chloride; the *hydrochloride* crystallises from water in lustrous, reddish-brown needles, and the *carbonate* is a brown, crystalline powder, readily losing carbonic anhydride when the aqueous solution is boiled. Aniline-aposafranine yields a *carbonate* as readily as aposafranine, carbonic anhydride precipitating the salt from an ethereal solution of the base in the form of a dark red, crystalline powder.

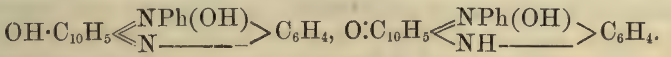
*Isorosinduline*, $NH_2\cdot C_{10}H_5 \lessdot \begin{array}{l} NPh(OH) \\ N\text{———} \end{array} > C_6H_4$, is produced on treating the more soluble of the above-mentioned hydrochlorides isomeric with acetylrosinduline hydrochloride with boiling dilute hydrochloric acid; the hydrolysis is more advantageously effected, however, by agitating a solution of the sulphite in sulphuric acid during the careful addition of water. The *hydrochloride* crystallises from water in long, lustrous, bluish-black needles, and melts and decomposes at 270°; the *platinochloride* is greenish-blue, and the *nitrate* crystallises in dark blue needles with bronze lustre. A comparison of the formulæ



$$\overset{4}{N}H_2\cdot C_{10}H_5 \lessdot \begin{array}{l} \overset{1}{N}\text{———} \\ \underset{2}{N}Ph(OH) \end{array} > C_6H_4 \text{ and } \overset{4}{N}H_2\cdot C_{10}H_5 \lessdot \begin{array}{l} \overset{1}{N}Ph(OH) \\ \underset{2}{N}\text{———} \end{array} > C_6H_4,$$

which represent rosinduline and isorosinduline respectively, explains the conversion of rosinduline bases into anhydrides, and also the fact that isorosinduline does not exhibit this property.

On boiling an aqueous solution of isorosinduline sulphate containing free sulphuric acid, the amido-group is replaced by hydroxyl, giving rise to the hydroxy-azonium *base*, $OH\cdot C_{10}H_5 \lessdot \begin{array}{l} NPh(OH) \\ N\text{———} \end{array} > C_6H_4$, which occurs in two forms, a blue and a red modification, yielding the same salts, which are red. The blue modification may be obtained in the manner indicated, or by hydrolysing acetylisorosinduline sulphite and rendering the liquid alkaline; it crystallises in lustrous, greenish-blue needles, melts and decomposes at 164°, and, although almost insoluble in cold water, yields a blue solution on boiling the liquid, which ultimately becomes turbid, owing to the production of the red modification. The *sulphate* crystallises readily, and rapidly decomposes in aqueous solution if no free acid is present; the *chloride*, $OH\cdot C_{10}H_5 \lessdot \begin{array}{l} NPhCl \\ N\text{———} \end{array} > C_6H_4$, crystallises in dark red leaflets, and yields the red modification on treatment with soda. The *platinochloride* crystallises in dark, reddish-brown needles. The red modification of the hydroxy-azonium base is immediately formed, on warming the freshly precipitated blue modification; it crystallises from alcohol in lustrous, black prisms, and when powdered is red, melting at the same temperature as the isomeride; it is insoluble in water and in cold dilute hydrochloric and sulphuric acids. Whilst the blue modification yields a dark green solution in concentrated sulphuric acid, the isomeride develops a cherry-red coloration with the solvent, but this liquid rapidly becomes green at 50—60°. From the behaviour of the bases, it seems clear that the red salts, obtained from both forms under the influence of acids, constitute the salts of the blue modification; dilute aqueous soda, however, also dissolves the isomerides, giving rise to the sodium derivative of the red base. The latter substance yields an *oxime*, whilst hydroxylamine has no action on the isomeride. The most reasonable explanation of the isomerism, therefore, is to be found in the following formulæ, depicting the constitution of the blue and red bases respectively.



$$OH{\cdot}C_{10}H_5<\begin{matrix}NPh(OH)\\N\text{———}\end{matrix}>C_6H_4,\quad O{:}C_{10}H_5<\begin{matrix}NPh(OH)\\NH\text{——}\end{matrix}>C_6H_4.$$

The author now develops a system of nomenclature to meet the requirements of the following substances.

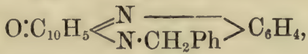
With M. TIKHVINSKY.—1 : 4-*Nitrobenzylaniline*,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2Ph,$$

is obtained by heating 1 : 4-chloronitrobenzene with benzylamine in a reflux apparatus for 10 hours at 180°; it crystallises from alcohol in golden-yellow prisms with blue reflex, and melts at 147°.

When acetamidonaphthaquinone (Abstr., 1895, i, 151) acts on benzylorthophenylenediamine, acetamidonaphthophenazine and benzylic chloride are not the only products. There is also formed *acetylbenzylrosinduline chloride*, and, on hydrolysing with dilute sulphuric acid, this is converted into *benzylrosinduline* (*benzylphenonaphthazime*).

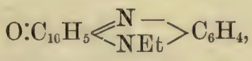
*Benzylrosindone* (*benzylphenonaphthazone*),



$$O{:}C_{10}H_5<\begin{matrix}N\text{——}\\N{\cdot}CH_2Ph\end{matrix}>C_6H_4,$$

is obtained by heating hydroxynaphthaquinone and benzylorthophenylenediamine hydrochloride with alcohol on the water bath, and treating the crystalline precipitate with boiling dilute caustic soda; it crystallises from toluene in two forms, which melt at 262—264°: short, dark red prisms with green lustre, or long, bright red needles. The solution in sulphuric acid is green.

With HERMANN FÜHNER.—*Ethylphenonaphthazone*,



$$O{:}C_{10}H_5<\begin{matrix}N\text{—}\\NEt\end{matrix}>C_6H_4,$$

is obtained by heating ethylorthophenylenediamine (1 mol.) with alcoholic hydroxynaphthaquinone for 12 hours; it crystallises from a mixture of benzene and alcohol, and melts at 192—193°. The solution in sulphuric acid is greenish-grey, and becomes orange-yellow on dilution, the *sulphate* separating in small, reddish-yellow needles.

2-*Hydroxyphenylphenazone*, $O{:}C_6H_4(OH)<\begin{matrix}N\text{—}\\NPh\end{matrix}>C_6H_4$, is formed when a concentrated aqueous solution of phenylorthophenylenediamine hydrochloride is added to dihydroxyquinone, freshly liberated by treating the ammonium derivative with hydrochloric acid; it crystallises in reddish-brown needles, and melts at 275—280°.

2-*Hydroxyethylphenazone*, $O{:}C_6H_4(OH)<\begin{matrix}N\text{—}\\NEt\end{matrix}>C_6H_4$, is obtained in the same way from ethylorthophenylenediamine, and crystallises from alcohol containing acetic acid in scarlet-red needles, melting at 230—240°.

1 : 2 : 3-*Methyldihydroxyphenazine*, $C_6HMe(OH)_2<\begin{matrix}N\\N\end{matrix}>C_6H_4$, or

1 : 2-*methylhydroxyphenazone*, $O{:}C_6HMe(OH)<\substack{N-\\NH}>C_6H_4$, is obtained as the *hydrochloride* when a hot solution of the ammonium derivative of dihydroxytoluquinone, acidified with hydrochloric acid, is allowed to remain with orthophenylenediamine hydrochloride; the base crystallises from alcohol in brick-red needles, and melts at 265—275°. 2 : 1- or 2 : 4-*Hydroxymethylphenylphenazone* is obtained in the same way from phenylorthophenylenediamine; it crystallises from glacial acetic acid in dark red leaflets with coppery lustre, and melts at 245—265°. 2 : 1- or 2 : 4-*Hydroxymethylethylphenazone* separates from a mixture of alcohol and benzene in red crystals with blue metallic lustre, and melts at 206°. 1 : 2- or 4 : 2-*Chlorhydroxymethylphenazone* crystallises from alcohol in large, brownish-red prisms, and melts at 200—201°. 1 : 2- or 4 : 2-*Chlorhydroxyethylphenazone* crystallises in short, dark red prisms, and melts at 215—216°. 1 : 2- or 4 : 2-*Chlorhydroxybenzylphenazone* crystallises from glacial acetic acid in scarlet needles, and melts at 234°.

M. O. F.

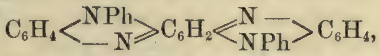
**Constitution of Fluorindines.** By FRIEDRICH KEHRMANN and H. BÜRGIN (*Ber.*, 1896, **29**, 1246—1254; compare Abstr., 1895, i, 526).—The formula for phenofluorindine suggested by Fischer and Hepp (Abstr., 1890, 1444) indicates the possible existence of mono- and dialkyl, and acidyl-imide derivatives, the authors' object was to test the validity of the formula by the preparation of such compounds.

Phenylmethylphenofluorindine, $C_6H_4<\substack{NH\\-\ N}>C_6HMe<\substack{N-\\NPh}>C_6H_4$, has been previously described (*loc. cit.*); the *platinochloride*,

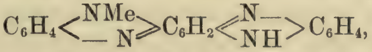
$$(C_{25}H_{18}N_4)_2,H_2PtCl_6,$$

is an indigo crystalline powder. When boiled with ethylic benzoate, the base yields the *benzoyl* derivative; this crystallises in dark red prisms of golden lustre, is insoluble in alcohol, and is readily hydrolysed by alcoholic sulphuric acid (50 per cent.); this method of preparing benzoyl derivatives is applicable to all monalkyl-fluorindines. The *hydrochloride* is readily soluble in alcohol, the solution is blue but not fluorescent, it crystallises in small, violet needles of coppery lustre, and readily regenerates the benzoyl derivative when heated at 110°, or by the action of ammonia on the alcoholic solution.

Phenylphenofluorindine, $C_6H_4<\substack{NH\\-\ N}>C_6H_2<\substack{N-\\NPh}>C_6H_4$, is prepared by the interaction of 2-hydroxyphenylphenazone, or the hydrochloride of the oxidation product of orthamidodiphenylamine, with orthophenylenediamine hydrochloride; it is identical with Fischer and Hepp's compound from aposafranine and orthophenylenediamine (this vol., i, 323) their statement (Abstr., 1895, i, 220) that diphenylphenofluorindine is formed from orthophenylenediamine and the oxidation product of orthamidodiphenylamine is, therefore, incorrect. The hydrochloride crystallises in canthradine green needles, and its alcoholic or sulphuric acid solution has a brownish-red fluorescence with a tinge of violet. The *benzoyl* derivative is obtained as a granular powder, and is less soluble than the base; the *hydrochloride* gives a blue nonfluorescent solution with alcohol, and in other respects resembles the corresponding compound described above. Fischer and Hepp describe the base as crystallising unchanged from ethylic benzoate.



Diphenylphenofluorindine, $C_6H_4<\substack{NPh\\ \text{—}N}>C_6H_2<\substack{N\text{—}\\ NPh}>C_6H_4$, prepared by the condensation of orthamidodiphenylamine with its oxidation product, is identical with the compound obtained by Fischer and Hepp from azophenine and mercuric oxide (Abstr., 1895, i, 220); the dihydrochloride is deposited in crystals of coppery lustre and differs from that of the monophenylfluorindine by its greater solubility in alcohol; the solution is blue with a violet-brown fluorescence; the addition of ammonia changes the colour to violet-red with a yellowish brick-red fluorescence which quickly disappears as the base is deposited.



*Methylphenofluorindine*, $C_6H_4<\substack{NMe\\ \text{—}N}>C_6H_2<\substack{N\text{—}\\ NH}>C_6H_4$, is prepared by heating at 260° the hydrochloride of the oxidation product of methylorthophenylenediamine with orthophenylenediamine hydrochloride and benzoic acid; it is probably identical with the compound prepared by Fischer and Hepp from orthodiamidophenazine and methylorthophenylenediamine; the base is a dark red, somewhat unstable, powder, the aqueous and alcoholic solutions of which are violet-red with a garnet-red fluorescence; the *dihydrochloride* crystallises in microscopic plates having a bronze lustre. J. B. T.

**Tropinic acid.** By GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1896, **29**, 1216—1218).—When tropinic acid is heated at 220° for 8 hours with hydriodic acid and phosphorus, it yields a base, the aurochloride of which forms yellow crystals melting at 208—210°. Although the composition of this salt is identical with that of piperidine aurochloride, and the melting point does not differ much from that of the latter, yet the crystals do not appear to be identical. The compound is being further examined. A. H.

**Quinine as a Developer.** By EDWIN ACKERMANN (*Bull. Soc. Chim.*, 1895, [3], **13**, 915—917).—On heating in a closed tube at 100° for 10 hours a mixture of 2 grams of quinine sulphate, 8 grams of zinc dust, and 40 c.c. of water, a liquid having strong reducing properties is obtained. This serves as an excellent developer, producing a clear and sharp image. J. F. T.

**Microscopic Discrimination of Cinchonidine and Homocinchonidine.** By TH. H. BEHRENS (*Zeit. anal. Chem.*, 1896, **35**, 133—143).—Hesse, whilst maintaining the individuality of homocinchonidine against Skraup, Claus, and de Vrij, who regard it as impure cinchonidine, has published methods for the conversion of the one into the other (Abstr., 1890, 1166). The author endeavours by microscopic methods to solve the question whether cinchonidine can, by the addition of other cinchona alkaloïds, be caused to assume the properties of homocinchonidine or the converse.

A 0·5 per cent. solution of the mixed hydrochlorides fractionally precipitated with sodium hydrogen carbonate deposits, first the cinchonidine in groups of filiform needles with a marked tendency to ramify at the ends (difference from cinchonine crystals, which do not ramify). Homocinchonidine yields broad, six-sided plates, and large stellate groups with broad foliated rays. Another method consists in subliming the bases and warming the sublimates with water until crusts begin to form. The same difference is observed as in the sodium carbonate precipitate. Still more distinct are the forms of the platinochlorides:—Cinchonidine yields minute spheroids which are at first clear and structureless, but gradually become turbid with radial fibrous crystals which rarely extend beyond the edge of the spheroid. Homocinchonidine yields large radiating dendrites and rosettes. A similar and highly characteristic difference is observed between the acid hydriodides.

The general tendency of homocinchonidine salts seems to be to form larger crystals than those of cinchonidine. Addition of quinine to a small crystallising cinchonidine salt does not cause it to furnish the large crystals of homocinchonidine. Fractional sublimation of mixtures of quinine, quinidine, and cinchonidine never yielded the characteristic crystals of homocinchonidine. Mixtures of quinine, quinidine, and homocinchonidine fractionally precipitated by sodium hydrogen carbonate never yielded the radiating, thread-like crystals of cinchonidine. Hesse's methods for the conversion of one alkaloïd into the other were repeated, but the characteristic crystalline forms of each substance were not affected. A great variety of specimens of commercial cinchonidine, homocinchonidine, and "quinetum" were examined by the fractionation methods and by precipitation with platinic chloride, and in all of them a proportion, frequently a preponderance, of the large, crystallising substance was found.

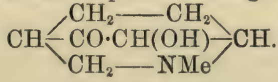
A plate of drawings of the microscopic crystals accompanies the paper. M. J. S.

**Scopolamine.** By Walter Luboldt (*Chem. Centr.*, 1895, ii, 896—897; compare Schmidt, Abstr., 1895, i, 158).—Crystallised scopolamine, $C_{17}H_{21}NO_4 + H_2O$, is best obtained from the hydrobromide; an aqueous solution of the latter, rendered alkaline with potassium carbonate, is extracted with chloroform, the solution evaporated, the residue extracted with ether, and the ethereal solution treated with the calculated quantity of water. It melts at 56°, and has a specific rotary power $[\alpha]_D = -14° 58'$ in aqueous and still lower in alcoholic solution.

When left in contact with concentrated sulphuric acid for a short time, water is withdrawn, but, on further contact, scopoline and atropic acid are produced. The author has obtained the compounds $C_{34}H_{40}N_2O_7,(HAuCl_4)_2$ and $(C_{17}H_{19}NO_3)_2,H_2PtCl_6$.

Scopoline, obtained from scopolamine by hydrolysing with baryta water, melts at 109°; the *hydrochloride*, *hydriodide*, *sulphate*, and *mandelate* (m. p. 112°) have been analysed. Concentrated hydriodic acid at 150—160°, concentrated sulphuric and acetic acids are without action on scopoline. On oxidation with potassium permanganate, the base yields a new compound, *scopoligenine*, which melts at 205—206°; its *aurochloride* melts at 235—236°; its *platinochloride* forms brown-red crystals; its *nitroso*-derivative melts at 174—175°, and, when treated with methylic iodide, is converted again into a scopoline salt.

Scopoline, when treated with methylic iodide, yields Hesse's scopolinemethylammonium iodide; the corresponding *chloride*, *aurochloride* (m. p. 246°), and *platinochloride* (m. p. 238°) are described. Scopolaminemethylammonium iodide, on treatment with silver oxide, yields *methylscopoline*, which boils at 244°, and with methylic iodide forms *methylscopolinemethylammonium iodide*, the *chloride* of which melts at 250°, the *aurochloride* at 191°, and the *platinochloride* at 243—244°. On treatment with potash, it is decomposed into a ketone, $C_7H_8O_2$, trimethylamine, water, and potassium iodide. The author gives a formula for scopoline analogous to Merling's formula for tropine, namely:



$$\mathrm{CH}\left\langle\begin{matrix}\mathrm{CH_2{-}{-}CH_2}\\ \mathrm{CO{\cdot}CH(OH)}\\ \mathrm{CH_2{-}{-}NMe}\end{matrix}\right\rangle\mathrm{CH}.$$

J. J. S.

**Albumoses.** By HUGO SCHRÖTTER (*Monatsh.*, 1896, **17**, 199—205; compare Henninger, Abstr., 1878, 802, 989).—The author has treated the albumoses previously obtained by him (Abstr., 1894, i, 215), their hydrochlorides, and also Paal's peptone hydrochloride with acetic anhydride, according to Henninger's method, and finds that the albumoses, but not the true peptones, yield products which are to be regarded not as regenerated albumin, as Henninger states, but as simple acetyl derivatives of albumoses. Henninger's assumption that peptones are formed by the addition of water to albumin is, therefore, no longer tenable. J. J. S.

**Saline Compounds of Caseïn and their Uses.** By FRANZ RÖHMANN (*Chem. Centr.*, 1895, ii, 684—685; from *Berl. Klin. Woch.*, **32**, 519—522).—Caseïn is a substance with acid properties, and dissolves in alkalis to form both acid and neutral salts. The alkali salts exhibit only a slight fluorescence; the acid calcium salt forms a milk-white solution; cow's milk probably owes its colour, to some extent, to the presence of this salt. Concentrated solutions of the sodium salt are readily precipitated by acetone, the calcium salt by alcohol; after washing with absolute alcohol and then with ether, the salts were obtained as white powders.

According to the author, the acid sodium salts (that is those acid to phenolphthaleïn) appear to be the most useful for diabetic purposes. With the aid of these salts, the author has obtained mixtures corresponding with cows' and human milk.

Caseïn silver is best precipitated by alcohol, and forms a white powder, which is readily soluble in warm water, giving a slightly opalescent solution. J. J. S.

**Reaction of Bilirubin with Iodine and Chloroform.** By JOHN L. W. THUDICHUM (*J. pr. Chem.*, 1896, [2], **53**, 314—324).—Half a gram of bilirubin was dissolved in rather more than a litre of chloroform, and an excess of a solution of iodine in absolute alcohol was added; the liquid became deep red, and if exposed to the light or warmed, a green substance separated, but this was not biliverdin. By shaking the chloroform solution with caustic soda and acidifying the extract, two violet compounds were isolated; the extracted chloroform solution was at first colourless, but speedily became rose coloured and then yielded a rose coloured substance by treatment with caustic soda. On distillation, the chloroform solution gave a volatile acrid yellow compound.

The foregoing experiment was made in view of Jolles's statement that bilirubin can be quantitatively oxidised to biliverdin by iodine in alcoholic solution. Jolles bases a long paper on this false premise (Abstr., 1894, ii, 466) and in consequence nearly all the conclusions contained therein are erroneous, as the author shows at some length.

A. G. B.

**Hæmatin.** By WILLIAM KÜSTER (*Ber.*, 1896, **29**, 821—824).—The author uses the term "hæmin" for the complex $C_{32}H_{31}ClN_4FeO_3$, and "hæmatin" for the substance derived from this by the action of alkalis, in which the chlorine has been replaced by OH. He has prepared a hæmatin acetate of the composition

$$(C_{32}H_{31}N_4FeO_3\cdot OAc)_4,CH_3\cdot COOH.$$

He has also obtained two specimens of hæmin with the composition $C_{32}H_{33}ClN_4FeO_3$ (one of them crystallised with $\frac{1}{6}$ mol. of amylic alcohol), and one specimen with $CH_2$ more than this, whilst a hæmatin bromide which he prepared had the composition $C_{31}H_{31}BrN_4FeO_3,EtOH$; the hæmin prepared by Cloëtta's method contains, as Cloëtta himself states, only 3 atoms of nitrogen.

By oxidising hæmatin, two new acids were obtained; namely, *dibasic hæmatic acid*, $C_8H_{10}O_5$, which melts at 112—113°, and yields, on further oxidation, the *anhydride of tribasic hæmatic acid;* this anhydride, $C_8H_8O_5$, melts at 94—95°. A third substance, which contains iron and is soluble in sodium carbonate, was also obtained.

C. F. B.

**A Phosphorised Constituent of Plant-seeds.** By ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1896, **22**, 90—94).—By extracting powdered seeds with a 10 per cent. solution of sodium chloride, a substance is precipitated with the proteïd at 80°, which goes into solution on cooling. It is free from nitrogen, but contains phosphorus (Palladin, Abstr., 1894, i, 631). Analysis gave the following result: C, 9·65; H, 2·83; and ash 67·88 per cent. Of the ash, more than half consists of phosphoric anhydride. The nature of the material is still uncertain. W. D. H.

# Organic Chemistry.

**Peculiar Decomposition of Diiodoacetylene.** By VICTOR MEYER and WILHELM PEMSEL (*Ber.*, 1896, **29**, 1411—1412).—Baeyer has shown (Abstr., 1885, 1199) that when diiodoacetylene is subjected to the action of light or heat, it is changed into a new substance melting at 184°. This is not, as he supposed, hexaiodobenzene, but tetraiodoethylene, $C_2I_4$; it crystallises in large prisms and melts, when pure, at 187° without decomposing, hence the specimen obtained by Homolka and Stoltz must have been impure, as it melted and decomposed about 165°.

The tetraiodoethylene is accompanied by a black, totally insoluble powder, containing a large proportion of carbon together with small quantities of iodine, hydrogen, and oxygen. A. L.

**Supposed Compound of Cyanoform and Mercuric Iodide.** By ANTONIO LONGI and G. MAZZOLINO (*Gazzetta*, 1896, **26**, i, 274—280). Pfankuch (this Journal, 1871, 901; 1873, 362) obtained a compound to which he assigned the composition $2CH(CN)_3,3HgI_2$, by heating mercuric cyanide, iodoform, and alcohol in a closed tube; Claus (*ibid.*, 1876, ii, 934), however, was unable to prepare this substance. By heating the three substances together at 150—160° for two days, hydrogen cyanide, carbonic oxide and anhydride, methane, an oil having the odour of an isonitrile, formic acid, and metallic mercury are obtained; from the product, the crystalline substance described by Pfankuch can be separated, but it consists of Boullay's double iodide having the composition $HgI_2,NH_4I,H_2O$. The double compound of cyanoform and mercuric iodide seems therefore not to exist.

W. J. P.

**Sodium Nitroferrocyanides.** By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1896, **12**, 146—168). *Trisodiumferrocyanide*,

$$Fe(CN)_5Na_3 + 6H_2O,$$

the mother substance of the series of compounds already described by the author (this vol., i, 197, 269), is obtained by adding phenylhydrazine (10 parts) to a mixture of sodium nitroferrocyanide (10 parts) and water (20 parts) cooled to −3°, when nitrogen is evolved. The mixture is allowed to remain two hours in the freezing bath, and then diluted with three times the volume of alcohol; this dissolves a red organic colouring matter which is formed and any unaltered sodium nitroferrocyanide, whilst a resinous, red substance remains behind. The latter is dissolved in air-cold water, mixed with a 10 per cent. solution of sodium hydroxide (20 c.c.), and precipitated with alcohol; the filtrate is mixed with more alcohol, and crystallised by prolonged cooling at 0°. The first precipitate is often contaminated with a small quantity of sodium ferrocyanide, the second precipitate is usually pure. It crystallises in reddish-yellow aggregates consisting of slender needles, gives an intense reddish-yellow solution with water, which, on addition of dilute acids, turns bright green. With ammonium sulphide it gives no coloration. When heated with hydroxylamine hydrochloride and sodium hydroxide, it gives a beautiful red coloration. When heated with sodium hydroxide, it is decomposed with formation of ferric hydroxide and sodium ferrocyanide, but no ammonia is evolved. With ferrous sulphate, it gives a bluish-white precipitate; with ferric chloride, a dark blue, and with sodium nitrite and acetic acid, a beautiful violet solution. When treated with a neutral solution of iodine, it is converted into a ferricyanide derivative, whereby 1 atom of iodine is used up for each atom of iron.

Trisodium ferrocyanide is very easily converted into sodium nitroferrocyanide by treating the aqueous solution with nitric oxide, or by mixing it with sodium nitrite. Since in the latter case no evolution of gas or heat takes place, the reaction must be considered as the formation of a double salt, and therefore the quaternary sodium nitroferrocyanide is expressed by the formula $Fe(CN)_5Na_3,NaNO_2$. Since secondary sodium nitroferrocyanide yields the quaternary salt when treated with sodium hydroxide, without oxidation or reduction taking place, it can be expressed by the formula $Fe(CN)_5NONa_2$. The compounds of nitroferrocyanic acid with alcohols, which have been already described are also double salts of the formula

$$Fe(CN)_5H_3,NO_2Me,H_2O, \&c.$$

*Sodium arseniteferrocyanide*, $Fe(CN)_5AsO_3Na_4H_2 + 9H_2O$ or $Fe(CN)_5AsO_2Na_4 + 10H_2O$, is obtained by adding a solution of sodium arsenite to a solution of sodium nitroferrocyanide containing sufficient sodium hydroxide for the formation of the quaternary salt. The solution is concentrated over sulphuric acid in a vacuum, the sodium arsenate which separates out being removed from time to time. It crystallises in microscopic, thin, yellow needles. The yellow aqueous solution gives no coloration with ammonium sulphide, and no ammonia with sodium hydroxide; with ferrous sulphate, a white precipitate, which turns bright blue on addition of hydrochloric acid; with ferric chloride, a beautiful violet solution, and when boiled with hydroxylamine hydrochloride and sodium hydroxide, an intense bluish-red solution. The *potassium* salt with $4H_2O$ crystallises in yellow aggregates, consisting of radiating needles. Both salts decolorise iodine and permanganate solutions. These compounds are analogous to the sulphite compound already described. Both are stable towards alkali cyanides at the ordinary temperatures, and when heated with alkali cyanide yield alkali ferrocyanide. The arsenite compound, when treated with sodium sulphite at the ordinary temperature, is converted into the sulphite compound. The author was unable to obtain analogous compounds with sodium antimonite, phosphite, or hypophosphite.

The sodium amidoferrocyanide, $Fe(CN)_5Na_3NH_2,6H_2O$, previously described by the author (this vol., i, 69), is an ammonium salt of the formula $Fe(CN)_5Na_3NH_3,6H_2O$, since it is easily obtained by the action of strong ammonia on trisodium ferrocyanide, and that without any evolution of gas. This ammonia compound is converted, without oxidation or reduction taking place, when treated with sodium nitrite, sodium sulphite, or sodium cyanide, into quaternary sodium nitroferrocyanide, sodium sulphite ferrocyanide, or sodium ferrocyanide respectively.

All the sodium nitroferrocyanides which contain the group $Fe(CN)_5$, yield a red colouring matter, when heated with hydroxylamine and sodium hydroxide. This is precipitated by alcohol as a red powder. It is soluble in water, not altered by zinc dust and sodium hydroxide, and decolorised by permanganate or dichromate solution, but the colour is again produced when heated with hydroxylamine and sodium hydroxide. When exposed to the air, it turns yellow, and is converted into the above ammonium compound

$$Fe(CN)_5Na_3NH_3,6H_2O.$$

The violet coloration produced by treating alkali sulphides with nitroferrocyanides is probably due to the formation of a reduction product, but the author was unable to isolate this in a satisfactory manner.

Sodium nitroferrocyanide, when treated with potassium cyanide, gives a beautiful, bluish-red coloration, and the solution shows a broad absorption band between the D and F lines, but all attempts to isolate the compound resulted in the formation of potassium ferrocyanide. E. C. R.

**Chloraloses.** By MAURICE HANRIOT (*Compt. rend.*, 1896, **122**, 1127—1129; compare Abstr., 1895, i, 321).—Galactose combines readily with chloral at 100° in presence of a small quantity of hydrochloric acid, and yields a mixture of α- and *β-galactochloral*, $C_8H_{11}Cl_3O_6$. The latter crystallises from water or methylic alcohol in nacreous lamellæ which melt at 202°, and do not sublime readily even under reduced pressure, and are almost insoluble in water or ether. It has no action on Fehling's solution, and gives a red coloration with a hydrochloric acid solution of orcinol. The *tetracetyl* derivative melts at 125°, and is insoluble in water or ether, but very soluble in alcohol and chloroform. The *tribenzoyl* derivative forms long needles, which melt at 141°, and dissolve in benzene and in methylic and ethylic alcohols.

When oxidised with permanganate, the galactochloral yields a chloralic acid, $C_7H_7Cl_3O_6$, which melts at 307°, and is identical with the acid obtained from arabinochloral.

Levulose, under similar conditions at 80°, yields *levulochloral*, $C_8H_{11}Cl_3O_6$, which crystallises in long needles melting at 228°, and is very soluble in hot water or alcohol. Its benzoyl derivative is amorphous. C. H. B.

**Separation of Methylamines.** By MARCEL DELÉPINE (*Compt. rend.*, 1896, **122**, 1064—1066).—The method is based on the observation of Henry that with formaldehyde, methylamine yields the compound $(CH_2\!:\!NMe)_3$ boiling at 166°, dimethylamine the compounds $OH\cdot CH_2\cdot NMe_2$ and $CH_2(NMe_2)_2$ boiling at 80—85°, whilst trimethylamine, the author assumes, remains unaltered, and continues to boil at 9°. The quaternary salt and any ammonium salts are removed by the known methods, and the vapour of the mixture of amines is passed into a well cooled 40 per cent. solution of formaldehyde. The product is then poured over an equal weight of potassium hydroxide, contained in a flask attached to a condenser the open end of which dips into a suitable solvent. The greater part of the trimethylamine volatilises and the residual liquid separates into two layers, the upper of which contains the mono- and di-methylamine derivatives. In consequence of the considerable differences in the boiling points, separation by fractionation presents no difficulties, and the amines are readily regenerated by the action of a boiling mixture of hydrochloric acid and alcohol. C. H. B.

**Oxime of Glucosamine Hydrochloride.** By ERNST WINTERSTEIN (*Ber.*, 1896, **29**, 1392—1393).—Glucosamine hydrochloride reacts with hydroxylamine to form the *oxime*, which crystallises in small masses of radiating, lustrous needles, and melts at 166°. The author proposes to study the configuration of this compound. A. H.

**Hydroxylamine Fumarate and its Products of Decomposition.** By SIMEON M. TANATAR (*Ber.*, 1896, **29**, 1477—1479).—*Hydroxylamine fumarate* is obtained in monoclinic needles by mixing cold concentrated aqueous solutions of hydroxylamine hydrochloride and potassium fumarate in equivalent quantities; when warmed in aqueous solution on the water bath, it loses carbonic anhydride, the ammonium salts of inactive aspartic and other acids being formed at the same time. C. F. B.

**α-Halogen Ketoximes.** By ROLAND SCHOLL and GEORG MATTHAIOPOULOS (*Ber.*, 1896, **29**, 1550—1558).—*Chloracetoxime*,

$$CH_2Cl\cdot CMe\!:\!NOH,$$

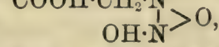
is obtained by treating chloracetone, prepared by Fritsch's method (Abstr., 1893, i, 303, and 1894, i, 490), with rather less than the theoretical amount of hydroxylamine hydrochloride and sodium carbonate. A little methylglyoxime, $NOH\!:\!CH\cdot CMe\!:\!NOH$, is always formed at the same time, and it is the only product if about three times the above quantity of hydroxylamine is used. Chloracetoxime boils at 71·2°, 84·5°, 98·0°, and 171° under 9, 21, 45, and 727 mm. pressure respectively, decomposing slightly at the last temperature. When its ethereal solution was treated with liquid nitric peroxide, a few crystals, melting at 167—168°, were obtained, but the main product was an unstable oil, doubtless *chloropropylpseudonitrole*, $CH_2Cl\cdot CMe(NO_2)\cdot NO$, which, when oxidised with chromic acid in acetic acid solution, yielded a small quantity of *chlorodinitropropane*, $CH_2Cl\cdot CMe(NO_2)_2$, boiling at 103—105° under 15·4 mm., and, with slight decomposition, at 200—202° (uncorr.) under atmospheric pressure. Attempts to convert the chloropseudonitrole into chloropropylene have been as yet unsuccessful.

*Bromacetoxime*, prepared in a similar manner, melts at 36·5°, and boils, without decomposition if small quantities are used, at 82·8° under 8 mm. pressure. It was less easy to obtain pure products from it than was the case with the chloro-compound. Bromacetone could probably be best obtained pure by the method described below in the case of iodacetone.

Iodacetone has been obtained pure for the first time by treating pure chloracetone with a concentrated aqueous solution of potassium iodide, and then adding methylic alcohol; it is a faintly yellowish liquid boiling at 58·4° under 11 mm. pressure. The *oxime* melts at 64·5°; when it is treated with nitric peroxide there is no sign of the formation of a pseudonitrile. C. F. B.

**Nitramineacetic acid.** By ARTHUR R. HANTZSCH and W. V. METCALF (*Ber.*, 1896, **29**, 1680—1685).—*Ethylic urethaneacetate*, $\mathrm{COOEt{\cdot}CH_2{\cdot}NH{\cdot}COOEt}$, prepared by Curtius' method from ethylic chlorocarbonate and ethylic amidoacetate, crystallises in long, colourless prisms, melting at 24·5—27°, and boiling at 145—146° (22 mm.); it is hygroscopic, and is only deposited in crystals if the solvent is anhydrous. The yield is 75—80 per cent. of the theoretical. *Urethaneacetic acid*, $\mathrm{COOH{\cdot}CH_2{\cdot}NH{\cdot}COOEt}$, prepared by the action of concentrated hydrochloric acid on the preceding compound, is crystalline, stable towards acids, decomposes carbonates, and melts at 67—69°. *Ethylic nitrosourethaneacetate*, $\mathrm{COOEt{\cdot}CH_2{\cdot}N(NO){\cdot}COOEt}$, obtained from the ethylic salt and nitrous anhydride, is a yellow, odourless oil, stable when pure, and volatile with steam; it is resolved into its constituents by the action of hydrochloric acid. *Ethylic nitrourethaneacetate* is formed by the action of concentrated nitric acid on the ethylic salt; it is a yellow oil, and with dry ammonia yields *ethylic nitramineacetate*, $\mathrm{COOEt{\cdot}CH_2{\cdot}N_2O_2H}$, which is crystalline, and melts at 24—25°; it decomposes carbonates, and is somewhat hygroscopic, but only dissolves slowly in water. The yield is about 90 per cent. of the theoretical. The salts are readily soluble; the *copper* salt forms well developed crystals; the *ammonium* salt melts and decomposes at about 60°. *Nitramineacetic acid* is obtained by the hydrolysis of the ethylic salt at low temperatures by means of either alkali or acid; it is dibasic, crystallises in long needles, and melts and decomposes at 103—104°. The *mercurous* and *lead* salts are sparingly soluble; the *potassium* and *silver* salts are crystalline and explosive, the latter darkens on exposure to light, and gives a mirror when boiled with water; the *copper* salt is deposited in blue crystals containing $2H_2O$. The salts and acid give a red coloration with ferric chloride, and the acid itself at 125° yields carbonic anhydride, nitrous oxide, and methylic alcohol, together with a substance which volatilises with difficulty, and is being further investigated; this indicates that the acid is probably not a true nitramine,

$$\mathrm{COOH{\cdot}CH_2{\cdot}NH{\cdot}NO_2},$$

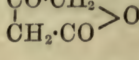
but a hydroxyl compound such as  $\left.\begin{array}{r}\mathrm{COOH{\cdot}CH_2{\cdot}N}\\ \mathrm{OH{\cdot}N}\end{array}\right>\mathrm{O}$, but acetic chloride, acetic anhydride, and phosphoric anhydride do not react with the acid at medium temperatures; when distilled with soda or baryta, carbonic anhydride and nitrogen are produced.

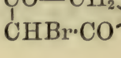
J. B. T.

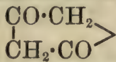
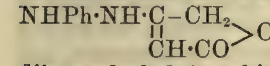
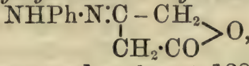
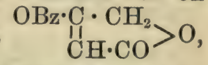
**Composition of Wool-fat. III.** By L. Darmstaedter and Isaac Lifschütz (*Ber.*, 1896, **29**, 1474—1477).—The residual wool-fat, left after the treatment described in the preceding communications (this vol., i, 198, 346), was treated with fusel oil, and the wool-wax so obtained was hydrolysed with alcoholic potash. From the product, the alcohols were separated by extraction with light petroleum; they amounted to 26—30 per cent. of the wax, and consisted of cetylic alcohol, melting at 76—77°, another alcohol melting at 66—68°, and cholesterol. The soaps were partly soluble in alcohol, partly insoluble. The insoluble part amounted to 33—36 per cent. of the wax. When cautiously treated with dilute hydrochloric acid, it yields *lanoceric acid*, $C_{30}H_{60}O_4$, apparently a dihydroxy-acid. This acid softens at 102°, and melts at 104—105°; it then solidifies again at 101—103°, and now melts again at the same temperature as before. It has, however, lost a molecule of water, probably from between the two hydroxyl groups, for it still has acid properties. The acid very readily forms a lactone, for example, when boiled with dilute hydrochloric acid, the lactone melts at 86°. When the acid is boiled with alcohol and strong hydrochloric acid, it is converted into a neutral substance, melting at 95—97°. C. F. B.

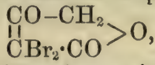
**Conversion of Tariric and Stearolic acids into Stearic acid.** By A. Arnaud (*Compt. rend.*, 1896, **122**, 1000).—Tariric and stearolic acids, $C_{18}H_{32}O_2$, are isomeric acids of the $C_nH_{2n-4}O_2$ series, but all attempts to convert them into stearic acid by hydrogenation have hitherto failed. If, however, one part of either acid is heated in sealed tubes at 200—210° with 10 parts of concentrated hydriodic acid and a small quantity of amorphous phosphorus, it yields a mixture of solid acids of the acetic series, from which stearic acid can be separated in considerable quantity by crystallisation from strong alcohol. C. H. B.

**Spectrochemical Investigation of the Ethereal Salts of $\alpha$- and $\beta$-Mesityloxidoxalic acid.** By Julius W. Brühl (*Annalen*, 1896, **291**, 137—146).—According to the accepted view of their constitution, the ethereal salts of $\alpha$-mesityloxidoxalic acid (Claisen, this vol., i, 561) should exhibit a higher molecular refraction and dispersion than the corresponding derivatives of the $\beta$-acid. The author's investigation shows that this is actually the case, and illustrates the influence of the solvent on the labile compounds under discussion. M. O. F.

**Tetronic acid.** By Ludwig Wolff [and Carl Schwabe] (*Annalen*, 1896, **291**, 226—252; compare this vol., i, 87, and 277).—It having been shown (*loc. cit.*) that tetric acid is a $\gamma$-lactone, it became desirable to prepare and investigate tetronic acid,  $\left.\begin{array}{l}CO{\cdot}CH_2\\ \vert\\ CH_2{\cdot}CO\end{array}\right>O$, the lactone of which tetric acid is a methyl derivative.

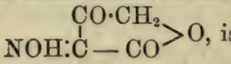
*Bromotetronic acid*,  $\left.\begin{array}{l}CO{-}CH_2\\ \vert\\ CHBr{\cdot}CO\end{array}\right>O$, is obtained by heating ethylic dibromacetoacetate under a pressure of 30—40 mm. during 2—3 hours at 120—130°; it crystallises from water in white needles or prisms, becomes yellow at 160°, and melts and decomposes at 183°. An aqueous solution develops a dark red coloration with ferric chloride, and a violet coloration with sodium nitrite; it reduces Fehling's solution and potassium permanganate, and liberates carbonic anhydride from carbonates. The *calcium* and *barium* salts dissolve readily in water, and crystallise in white needles or prisms; the *silver* salt crystallises from water in slender needles.

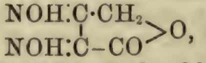
*Tetronic acid*,  $\begin{array}{l}\mathrm{CO{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CO}\end{array}\!>\!\mathrm{O}$, is prepared by reducing bromotetronic acid with sodium amalgam in an atmosphere of carbonic anhydride, and crystallises from a mixture of alcohol and petroleum in lustrous plates, and from warm water in prisms; it sinters at 135°, and melts at 141°. Its behaviour towards ferric chloride, sodium nitrite, Fehling's solution, and potassium permanganate is the same as that of the bromo-derivative. The *calcium* salt contains $2\frac{1}{2}H_2O$, but can be crystallised in needles, which contain $4H_2O$, and lose $1\frac{1}{2}$ mol. on exposure to air; the *copper* salt crystallises in green needles, and the *silver* salt dissolves readily in water. When the reduction of bromotetronic acid is carried out in the ordinary manner, and carbonic anhydride is not led into the liquid, an *acid* of the formula $C_{10}H_{10}O_6$ is produced; it crystallises from hot water in vitreous needles or prisms, melts and evolves gas at 209°, and develops no coloration with ferric chloride or sodium nitrite. The *phenylhydrazide* or *hydrazone* of tetronic acid,  $\begin{array}{l}\mathrm{NHPh{\cdot}NH{\cdot}C{-}CH_2}\\ \qquad\qquad\;\;\mathrm{CH{\cdot}CO}\end{array}\!>\!\mathrm{O}$, or  $\begin{array}{l}\mathrm{NHPh{\cdot}N{:}C{-}CH_2}\\ \qquad\qquad\mathrm{CH_2{\cdot}CO}\end{array}\!>\!\mathrm{O}$, crystallises from dilute alcohol in white prisms, and melts at 128°; the solution in concentrated sulphuric acid is bluish-violet, and becomes red on adding potassium dichromate. *Benzoyltetronic acid*,  $\begin{array}{l}\mathrm{OBz{\cdot}C{\cdot}CH_2}\\ \qquad\mathrm{CH{\cdot}CO}\end{array}\!>\!\mathrm{O}$, is obtained by agitating aqueous tetronic acid with benzoic chloride and sodium carbonate; it crystallises from a mixture of chloroform and petroleum in lustrous leaflets or prisms, and melts at 120°.

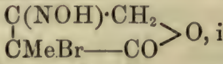
*Dibromotetronic acid*,  $\begin{array}{l}\mathrm{CO{-}CH_2}\\ \mathrm{CBr_2{\cdot}CO}\end{array}\!>\!\mathrm{O}$, is obtained by treating a solution of tetronic acid in chloroform with bromine in presence of water, bromotetronic acid being produced when this agent is absent. The acid, however, is unstable, and undergoes spontaneous conversion into a mixture of tribromomethylketole, bromotetronic acid, and, possibly, dibromomethylketole. Alkali carbonates decompose dibromotetronic acid, giving rise to bromoform.

*Tribromomethylketole*, $\mathrm{CBr_3{\cdot}CO{\cdot}CH_2{\cdot}OH}$, is obtained by adding bromine to bromotetronic acid suspended in water, and heating the liquid on the water bath until carbonic anhydride ceases to be evolved; it crystallises from acetone or methylic alcohol in lustrous, rhombic leaflets, which sinter at 168°, and melt, evolving gas, at 174°. Fehling's solution and potassium permanganate are reduced when gently heated, and hot sodium carbonate resolves the substance into bromoform and glycollic acid; bromoform obtained in this way melts at 9°, and boils at 146°. When concentrated ammonia acts on dibromotetronic acid, dibromacetamide is produced.

*α-Dibromethylketole*, $CBr_2Me\cdot CO\cdot CH_2\cdot OH$, is produced when bromine is added to methyltetronic acid suspended in water, and the liquid heated on the water bath until the evolution of carbonic anhydride ceases; it crystallises from a mixture of chloroform and petroleum in lustrous leaflets, and melts at 85°. It quickly reduces Fehling's solution and an ammoniacal solution of silver.

*Oximidotetronic acid*,  $\begin{array}{l} CO\cdot CH_2 \\ NOH:C-CO \end{array}>O$, is obtained by acidifying with hydrochloric acid a solution of sodium nitrite in which tetronic acid has been suspended during 15 minutes; it crystallises from water in yellow leaflets, and melts at 136° evolving gas, or when rapidly heated, at 144°. It is strongly acidic, and the alkali salts are deep violet, and the *silver* salt separates in crystals having a greenish lustre. The acid is an unstable substance, and becomes brown when exposed to light; boiling water eliminates hydrogen cyanide. Whilst nitrous acid converts methyltetronic acid into α-oximidopropionylglycollic acid (this vol., i, 88), bromotetronic acid yields oximidotetronic acid; dibromotetronic acid is also produced, arising from the action of hypobromous acid on bromotetronic acid.

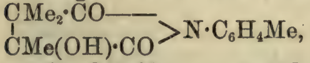
*Dioximidobutyrolactone*,  $\begin{array}{l} NOH:C\cdot CH_2 \\ NOH:C-CO \end{array}>O$, slowly separates from a solution of oximidotetronic acid in hydrochloric acid, and crystallises from water in lustrous prisms containing $1H_2O$; the water is removed at 100°, and the anhydrous substance becomes brown and melts, evolving gas, at 178°. The dioxime is acidic in character, and forms several crystalline metallic derivatives.

*Oximidobromomethylbutyrolactone*,  $\begin{array}{l} C(NOH)\cdot CH_2 \\ CMeBr-CO \end{array}>O$, is obtained by the action of hydroxylamine on finely powdered bromomethyltetronic acid suspended in water; it crystallises from a mixture of ether and petroleum in large, transparent prisms, and melts at 128°. The substance is feebly acidic, and dissolves slowly in soda and ammonia; it is decomposed by water at 80—90°, yielding diacetyl, carbonic anhydride, and brominated products.

*Anhydrotetronic acid*, $C_8H_6O_5$, is produced when a concentrated aqueous solution of tetronic acid is heated on the water bath, and allowed to remain at ordinary temperatures during one or two weeks; it is much less readily soluble in water than tetronic acid, and crystallises in aggregates of white needles, which contain $1H_2O$. It becomes yellow at 240—245°, and melts at 263°, at which temperature it decomposes completely. The aqueous solution develops a red coloration with ferric chloride, and becomes yellow with sodium nitrite, or reddish-brown if the solution is concentrated. The *barium* salt crystallises in slender needles containing $5H_2O$, and dissolves readily in water; the *calcium* salt also contains $5H_2O$, and crystallises in needles, being less readily soluble than the barium salt.

M. O. F.

**Hydroxytrimethylsuccinic acid.** By KARL AUWERS and G. VON CAMPENHAUSEN (*Ber.*, 1896, **29**, 1543—1549).—*Hydroxytrimethylsuccinic acid*, $COOH\cdot CMe_2\cdot CMe(OH)\cdot COOH$, is obtained from the cyanhydrin of ethylic dimethylacetoacetate; an ethereal solution of this substance is poured on to a large excess (five times the theoretical amount) of powdered potassium cyanide, just moistened with water, and strong hydrochloric acid is added, drop by drop, in amount equivalent to the cyanide. After 24 hours, the ethereal solution is poured into three times its volume of strong hydrochloric acid, filtered after 24 hours, then heated for several hours on the water bath, and finally evaporated to dryness, the residue being extracted with ethylic acetate. It melts at 153—154° when heated slowly, at 159—160° when heated quickly; at a higher temperature, it appears to form the anhydride, which distils over at about 240°. With acetic chloride, it yields the *acetyl* derivative, not of the acid, but *of the anhydride;* this melts at 67—68°. With aniline, it yields an *anil* melting at 145—146°; with paratoluidine, the corresponding *tolil*,



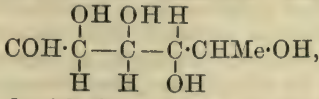
$\begin{matrix}\text{CMe}_2\cdot\text{CO}\text{——}\\ |\\ \text{CMe(OH)}\cdot\text{CO}\end{matrix}\!>\!\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, melting at 184—185°; this yields, with acetic chloride, an *acetyl* derivative melting at 131°, which, when heated with alcoholic potash, does not lose its acetyl group, but yields the *acetyl* derivative of the *tolilic acid*,

$$COOH\cdot CMe_2\cdot CMe(OAc)\cdot CO\cdot NH\cdot C_6H_4Me,$$

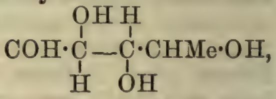
which melts at 156—157° when heated slowly, at 160° when heated quickly (at which end of the chain the tolylamido-group is situated is, of course, uncertain). When strong alcoholic potash (20 per cent.) is used, a substance, melting at 108—108·5°, and insoluble in alkalis and acids, is obtained; and G. Komppa, who is also engaged in investigating hydroxytrimethylsuccinic acid, even seems to have obtained the normal product of hydrolysis, the tolil. The acetyltolilic acid, after it has been melted and allowed to solidify again in a melting-point tube, then melts at 185°, being, apparently, converted into the tolil; if, however, a larger quantity is heated for a short time above its melting point, the acetyltolyl, melting at 131°, is obtained.

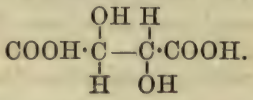
C. F. B.

**The Configuration of Dextrotartaric acid.** By EMIL FISCHER (*Ber.*, 1896, **29**, 1377—1383).—The formula of dextrotartaric acid, with reference to the formulæ employed for the various members of the sugar group, can be ascertained by converting rhamnose, the constitution of which with reference to that of the glucoses is known, into methyltetrose by Wohl's method, and then treating the latter with nitric acid. Dextrotartaric acid is thus produced, and its configuration follows from that of rhamnose. The latter has the stereochemical formula



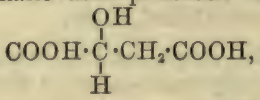
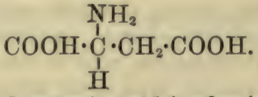
$\text{COH}\cdot\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}-\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}-\underset{\text{OH}}{\overset{\text{H}}{\text{C}}}\cdot\text{CHMe}\cdot\text{OH}$, the configuration of the groups combined with the $\delta$-carbon atom being unknown (Abstr., 1894, i, 218).

*Tetracetylrhamnonic nitrile*, $CH_3\cdot[CH\cdot OAc]_4\cdot CN$, is obtained by treating the oxime with acetic anhydride and sodium acetate. It is moderately soluble in hot water, crystallises from alcohol in large, transparent crystals, and melts at 69—70°. When it is treated with an ammoniacal solution of silver oxide, it yields the *acetamide compound of methyltetrose*, $CH_3{\cdot}[CH{\cdot}OH]_3{\cdot}CH(NHAc)_2$, which crystallises from water in colourless prisms, and melts at 201—205° (corr.); it does not reduce Fehling's solution. *Methyltetrose* forms slender, yellow needles, and melts somewhat indefinitely between 171° and 174° (uncorr.). It has the configuration  $\mathrm{COH{\cdot}}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\mathrm{—}\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\mathrm{{\cdot}CHMe{\cdot}OH}$, as is shown by its formation from rhamnose. When methyltetrose or its acetamide compound is treated with nitric acid, it yields dextrotartaric acid, which must, therefore, have the configuration



$$\mathrm{COOH{\cdot}}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\mathrm{—}\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\mathrm{{\cdot}COOH.}$$

This oxidation of methyltetrose with formation of dextrotartaric acid is precisely similar to the formation of *l*-trihydroxyglutaric acid from rhamnose, and of mucic acid from rhamnohexonic acid.

It follows from the configuration of *d*-tartaric acid that the formula of the malic acid produced from it by the action of hydriodic acid, must be  $\mathrm{COOH{\cdot}}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\mathrm{{\cdot}CH_2{\cdot}COOH}$, whilst that of the corresponding aspartic acid must be  $\mathrm{COOH{\cdot}}\underset{\mathrm{H}}{\overset{\mathrm{NH_2}}{\mathrm{C}}}\mathrm{{\cdot}CH_2{\cdot}COOH.}$

This formula for *d*-tartaric acid is also in complete agreement with the fact that *d*-saccharic acid yields *d*-tartaric acid on oxidation (Fischer and Crossley, Abstr., 1894, i, 230). A. H.

**Racemism. XIV.** By Isidor Traube (*Ber.*, 1896, **29**, 1394—1397).—The application of the molecular volumetric method of determining molecular weights to optically active and inactive substances shows that in every case which has been examined, the three forms, dextro- and lævo-rotatory, and racemic, all have approximately the same molecular weight. In the case of substances such as hydrocarbons, ethereal salts, and ethers, they are all monomolecular, and the racemic form must be looked on as a mixture of the two optically opposed forms. This is the case with the ethylic tartrates, *d*- and *l*-limonene and dipentene, and the three carvones. Dextrotartaric acid and racemic acid, on the other hand, have both of them the double molecular weight, and it is probable that the formation of racemic acid from dextro- and lævo-tartaric acids, is represented by the equation $dd + ll = 2dl$. In other cases, the average molecular weight appears to be intermediate between those corresponding with the single and the double formula. For isoamylic alcohol it has the ratio 1·52 to the single formula; whilst with coniïne the ratio is 1·6.

A. H.

**Formation of Carbon Chains. X. Condensations which should yield an Ethereal Salt of Methylacetylenetetracarboxylic [1 : 1 : 2 : 2-Propanetetracarboxylic] acid.** By CARL A. BISCHOFF (*Ber.*, 1896, **29**, 1504—1514).—Ethylic propanetetracarboxylate should be formed as the normal product of the following reactions.

I. $CMeNa(COOR)_2 + CHX(COOR)_2 =$
$NaX + CMe(COOR)_2{\cdot}CH(COOR)_2$.

II. $CMeX(COOR)_2 + CHNa(COOR)_2 =$
$NaX + CMe(COOR)_2{\cdot}CH(COOR)_2$.

R being either a methyl or an ethyl group and X a chlorine or bromine atom.

(1) In the first case, namely, in the condensation of methylic sodiomethylmalonate and methylic chloromalonate, the chief products isolated were methylic ethanetetracarboxylate and the unsaturated methylic ethylenetetracarboxylate, from which succinic and fumaric acids respectively were produced. Methylsuccinic acid, which would have been produced from any methylic propanetetracarboxylate formed, could not be isolated.

This reaction is, therefore, abnormal, 2 mols. of methylic sodiomethylmalonate condensing with 2 mols. of the chloro-compound with the formation of the unsaturated methylic ethylenetetracarboxylate and regeneration of methylic methylmalonate; at the same time 3 mols. of the methylic chloromalonate react with 3 mols. of sodium methoxide with the production of methylic ethanetetracarboxylate and methylic dimethoxymalonate.

(2) The condensation between methylic sodiomethylmalonate and methylic bromomalonate also proceeds abnormally, a trace of the normal product, however, being produced; the reaction otherwise proceeds somewhat differently to that of the chloro-compound, the methylic bromomalonate being, for the most part, converted into the methylic propanehexacarboxylate.

Employing the ethylic salts instead of the methylic in the previous experiments, the reaction between ethylic sodiomethylmalonate and ethylic chloromalonate was found to proceed abnormally; with the bromo-compound, a certain quantity of the normal product was, however, isolated.

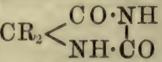
The condensation between ethylic sodiomalonate and ethylic chloromethylmalonate also yielded none of the normal product, whilst with ethylic bromomethylmalonate a product was obtained which yielded propanetricarboxylic acid on hydrolysis, and was evidently the normal condensation product, ethylic propanetetracarboxylate.

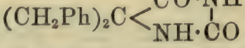
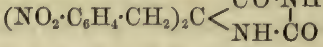
J. F. T.

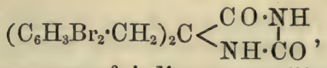
**Formation of Carbon Chains. XI. Condensations which should yield an Ethereal Salt of Ethylacetylenetetracarboxylic [1 : 1 : 2 : 2-Butanetetracarboxylic] acid.** By CARL A. BISCHOFF (*Ber.*, 1896, **29**, 1514—1521).—The condensation between ethylic bromomalonate and ethylic sodethylmalonate, both in alcoholic and in xylene solutions, yields ethylic ethylenetetracarboxylate, the corresponding chloro-compound, however, only gives this product in alcoholic solution, whilst in xylene, ethylic ethanetetracarboxylate is formed. Condensations between ethylic sodiomalonate and ethylic chlorethylmalonate, ethylic sodiomalonate and ethylic bromomalonate, ethylic sodethylmalonate and ethylic chloro- and bromomalonates (in both alcohol and xylene), were in no case found to yield the normal product. J. F. T.

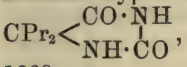
**Synthesis of Carbamide and symmetrical complex Carbamides.** By PAUL CAZENEUVE (*Compt. rend.*, 1896, **122**, 999—1000). —When guaiacol carbonate is mixed with alcohol of 93° saturated with ammonia, it is rapidly converted into carbamide with liberation of guaiacol. The reaction is analogous to that of ammonia on ethylic carbonate, and it confirms the view that the guaiacol carbonate, $CO(O\cdot C_6H_4\cdot OMe)_2$, has the function of an ethereal salt.

Similarly, guaiacol carbonate yields diphenylcarbamide when heated with aniline, and the corresponding symmetrical carbamides when heated with orthotoluidine and paratoluidine. C. H. B.

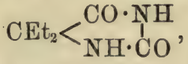
**α-Dialkylhydantoïns.** By GIORGIO ERRERA (*Gazzetta*, 1896, **26**, i, 197—211).—On treating cyanacetamide in alcoholic solution with sodium ethoxide, the two methylenic hydrogen atoms are displaced by sodium, and a crystalline, white *disodio*-derivative is deposited; the latter, when treated with an alkylic iodide, yields an α-dialkylcyanacetamide, which is acted on in a twofold manner by alkaline hypobromite; the CN group is hydrated, and becomes a $-CO\cdot NH_2$ group, whilst the original $-CO\cdot NH_2$ is oxidised to the isocyanic group $-NCO$, in accordance with Hofmann's reaction. The reaction, however, does not end with the formation of the compound $CONH_2\cdot CR_2\cdot NCO$ from $CN\cdot CR_2\cdot CONH_2$, but the amido and isocyanic groups join to form the hydantoïn derivative,  $CR_2<\begin{matrix}CO\cdot NH\\ NH\cdot \overset{|}{C}O\end{matrix}$. Hydantoïn itself cannot be prepared by the action of hypobromite on cyanacetamide, because the methylene group becomes attacked and the molecule splits up.

*Dibenzylcyanacetamide*, $CN\cdot C(CH_2Ph)_2\cdot CONH_2$, is readily obtained by heating cyanacetamide, to which sodium ethoxide has been added, with benzylic chloride on the water bath; it crystallises in colourless, rhombic tablets melting at 165°, and is soluble in hot alcohol; $a : b : c = 0{\cdot}2880 : 1 : 0{\cdot}30674$. On fusion with dehydrating agents, such as phosphoric anhydride, it yields the nitrile of dibenzylmalonic acid, whilst, if the finely powdered amine is heated at 100° with a potash solution of bromine, it is converted into *α-dibenzylhydantoïn*,  $(CH_2Ph)_2C<\begin{matrix}CO\cdot NH\\ NH\cdot \overset{|}{C}O\end{matrix}$, which can be purified by dissolving in soda and precipitating the filtered solution with acid. It crystallises in lustrous, colourless laminæ, melting at 208—209°, and dissolves in caustic alkalis, but not in alkaline carbonates. Its *dinitro*-derivative,  $(NO_2\cdot C_6H_4\cdot CH_2)_2C<\begin{matrix}CO\cdot NH\\ NH\cdot \overset{|}{C}O\end{matrix}$, is obtained by boiling with fuming nitric acid, and crystallises in yellow laminæ melting and decomposing at 285°; the nitro- and methylene-groups are probably in the para-position.

*α-Tetrabromodibenzylhydantoïn*,  $(C_6H_3Br_2\cdot CH_2)_2C<\begin{array}{l}CO\cdot NH\\ NH\cdot CO\end{array}$, obtained by direct bromination in presence of iodine, crystallises in white laminæ melting at 285°; it dissolves readily in caustic alkalis, and is possibly a mixture of isomerides.

*Dipropylcyanacetamide*, $CN\cdot CPr_2\cdot CONH_2$, prepared with the aid of propylic bromide, forms white crystals melting at 152—153°; alkaline hypobromite readily converts it into *α-dipropylhydantoïn*,  $CPr_2<\begin{array}{l}CO\cdot NH\\ NH\cdot CO\end{array}$, which crystallises in colourless laminæ melting at 199°.

*Diethylcyanacetamide*, $CN\cdot CEt_2\cdot CONH_2$, prepared with the aid of ethylic iodide, forms irregular, colourless crystals melting at 121°; with alkaline hypobromite, it yields *α-diethylhydantoïn*,



$$CEt_2<\begin{array}{l}CO\cdot NH\\ NH\cdot CO\end{array},$$

which crystallises in large, colourless, rhombic prisms melting at 165°; $a : b : c = 0{\cdot}83910 : 1 : 2{\cdot}51715$.

*Dimethylcyanacetamide*, $CN\cdot CMe_2\cdot CONH_2$, crystallises in colourless, triclinic laminæ melting at 105—106°;

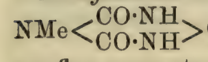
$$a : b : c = 1{\cdot}065485 : 1 : 1{\cdot}18805.$$

$\alpha = 76°\ 42'$, $\beta = 50°\ 8'$, $\gamma = 67°\ 33'$. The α-dimethylhydantoïn obtained from it melts at 173—174°, not at 175°, as Urech's preparation did (Abstr., 1873, 59). W. J. P.

**Benzylidenebiuret and Allied Compounds.** By Hugo Schiff (*Annalen*, 1896, **291**, 367—377).—*Benzylidenedicarbamide*,

$$CHPh(NH\cdot CO\cdot NH_2)_2,$$

is produced by heating carbamide with benzaldehyde; it melts at 200°, and when heated at 220—230°, yields benzaldehyde, water, ammonia, and ammonium carbonate, the residue consisting of cyanuric acid and benzylidenebiuret (compare Abstr., 1894, i, 374).

*Benzylidenemethylbiuret*, which probably has the constitution  $NMe<\begin{array}{l}CO\cdot NH\\ CO\cdot NH\end{array}>CHPh$, is obtained by heating benzylidenebiuret in a reflux apparatus with alkali and the alkylic iodide, although biuret does not yield alkyl derivatives under these conditions; it separates from water in colourless, prismatic needles, and melts at 238°. *Benzylideneethylbiuret* crystallises from water, and melts at 250°.

*Benzylidenebismethylcarbamide*, $CHPh(NH\cdot CO\cdot NHMe)$, is produced on adding a few drops of concentrated hydrochloric acid to an alcoholic solution of methylcarbamide and benzaldehyde; it crystallises in needles, and melts at 187—188°. When heated at 250°, it yields methylamine, ammonia, ammonium carbonate, benzaldehyde, and water, a small quantity of benzylidenemethylbiuret being also produced.

Hofmann observed the formation of dimethylcyanuric acid on distilling methylacetylcarbamide; the substance is also produced when methylcarbamide is heated with benzaldehyde at 220°. It is probable that trimethylcyanuric acid is formed at the same time.

According to the statement of Wilm and Wischin (*Annalen*, 1868, **147**, 155), carbamide unites with ethylic chlorocarbonate, forming ethylic allophanate; the reaction, however, is not a simple one. When a mixture in molecular proportion is heated in a reflux apparatus during two or three hours, one-third of the salt undergoes no change; a crystalline solid is produced composed of cyanuric acid and ammonium chloride along with a trace of biuret, but no ethylic allophanate is formed. When double the proportion of carbamide is employed, it yields one-sixth of its weight of ethylic allophanate, along with cyanuric acid, ammonium chloride, and a very small quantity of biuret.

*Carbonyldicarbamide*, $CO(NH\cdot CO\cdot NH_2)_2$, is formed when carbamide is heated with a 20 per cent. solution of carbonyl dichloride in toluene, the temperature being maintained at 100° during two days; it crystallises from water in lustrous scales, and melts at 231—232°. Further treatment with carbonyl dichloride gives rise, as Schmidt has pointed out, to cyanuric acid, and carbonyldibiuret is produced in the same way (compare Archdeacon and Cohen (Proc., 1895, 148).

Determinations of the solubility of cyanuric acid are given; one part of the anhydrous acid dissolves in about 800 parts of water at ordinary temperatures. M. O. F.

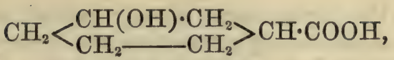
**Acetylbiuret and Benzoylbiuret.** By Adriano Ostrogovich (*Annalen*, 1896, **291**, 377—380).—*Acetylbiuret*,

$$NH_2\cdot CO\cdot NH\cdot CO\cdot NHAc,$$

is obtained when anhydrous biuret and acetic chloride are heated during one hour in sealed tubes at 100°; it crystallises from water in flat, nacreous needles, and melts at 193—193·5°. The substance is also formed on heating carbamide with acetylurethane (compare this vol., i, 261). An attempt to produce this substance by the action of ammonia on ethylic acetylallophanate at 50° resulted in the formation of ethylic allophanate and acetamide; when alcoholic ammonia is employed, and the temperature raised to 100°, biuret and acetamide are produced.

*Benzoylbiuret* separates from boiling water as a colourless, crystalline powder, and melts and decomposes at 228—230°. Concentrated alcoholic or aqueous ammonia at 40—50° converts ethylic benzoylallophanate into ethylic allophanate and benzamide, whilst, at 100°, benzamide and biuret are produced. M. O. F.

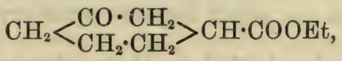
**Reduction of Phenolcarboxylic acids. II.** By Alfred Einhorn [and Franz Coblitz] (*Annalen*, 1896, **291**, 297—304; compare this vol., i, 45).—3 : 1-*Hydroxyhexamethylenecarboxylic acid*,



$$CH_2<\begin{matrix}CH(OH)\cdot CH_2\\ CH_2\text{———}CH_2\end{matrix}>CH\cdot COOH,$$

is obtained by slowly adding sodium to a boiling solution of metahydroxybenzoic acid in absolute alcohol, and crystallises from ethylic acetate in leaflets melting at 132°; the *barium* salt contains $1H_2O$, and the *copper* salt is a green powder, dissolving readily in water and alcohol. The *methylic* and *ethylic* salts are colourless liquids of agreeable odour, boiling at 140—150° and 148—158° respectively under a pressure of 14 mm.; the *amide* crystallises from water in white leaflets, and melts at 161°. When diazobenzene chloride (2 mols.) is added to an aqueous solution of the sodium salt, the *compound* $C_{19}H_{16}N_4O$, is produced; it crystallises from alcohol in lustrous, red needles, and melts at 131°, dissolving in concentrated sulphuric acid, with development of a dark red coloration.

*Ethylic* 3 : 1-*ketohexamethylenecarboxylate*,



$$CH_2<\begin{matrix}CO\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot COOEt,$$

is formed when ethylic 3 : 1-hydroxyhexamethylenecarboxylate is oxidised with sodium dichromate and sulphuric acid; it is a colourless liquid of agreeable odour, and boils at 170—180° under a pressure of 16 mm. Hydrolysis gives rise to the acid, which has been already obtained by von Baeyer and Tutein on eliminating carbonic anhydride from hydroxytetrahydroterephthalic acid (Abstr., 1889, 1180). M. O. F.

**Action of Bromine on Aromatic Iodo-compounds.** By H. Hirtz (*Ber.*, 1896, **29**, 1404—1411).—When bromine acts on aromatic iodo-compounds, the iodine is seldom replaced by bromine, as is the general rule in the aliphatic series, and there is no formation of additive compounds (iododibromides), as is the case when chlorine is used; in the majority of cases a simple substitution product is formed.

Bromine acts on iodobenzene in much the same manner as on benzene itself, and forms 1 : 4-bromiodobenzene. Pariodotoluene is but slowly attacked by bromine, and even when excess of halogen is used, the action is still incomplete; the product, 2 : 4-*bromiodotoluene*, $C_7H_6BrI$, is an oil boiling at 250—265° (uncorr.), which, on dissolution in cold, fuming nitric acid, yields a 2 : 4 : 2-*bromiodonitrotoluene*, $C_7H_5BrI\cdot NO_2$; this crystallises from alcohol in bright yellow needles, and melts at 92°. Metiodotoluene is rapidly acted on by bromine, and the reaction must be carried out at as low a temperature as possible; the *product* is an oil, which boils at 255—265° (uncorr.), and, when heated with a mixture of fuming nitric and sulphuric acids, yields a *bromometiododinitrotoluene*, $C_7H_4BrI(NO_2)_2$, which crystallises from acetic acid, and forms fine, bright yellow needles, melting at 139—141°. With regard to its behaviour towards bromine, orthiodotoluene is intermediate in character between the meta- and para-compounds, the interaction taking place somewhat readily with the production of a *bromiodotoluene* [probably 2 : 4] boiling at 262—266°.

Pariodobenzoic acid is not attacked at ordinary temperatures, but at a temperature of 160—180° the iodine is replaced by bromine;

whilst at 125° the replacement is only partial, and the two acids present may be separated by converting the iodo-compound into the iododichloride, which is insoluble in acetic acid. Under no conditions does the bromine act as a substituting agent. The behaviour of metiodobenzoic acid closely resembles that of the para-acid. Orthoiodobenzoic acid, however, yields a mixture of substances which, by the action of chlorine, yields the orthiododichloride of parabromobenzoic acid; the mother liquor from the latter substance, when treated with caustic soda, yields the sodium salts of orthiodosobenzoic acid and a mixture of several bromobenzoic acids.

Bromine acts with explosive energy on α-iodonaphthalene, yielding bromiodonaphthalene [probably 1 : 4], melting at 85·5°. β-Iodonaphthalene is also violently attacked, and yields a mixed product; the latter, on treatment with chlorine, affords an iododichloride, which on reduction gives a *bromo-β-iodonaphthalene*, which crystallises from dilute alcohol, and melts at 55°; the mother liquor from the iodochloride yields a dark oil, which deposits white crystals of 1 : 2-bromiodonaphthalene.

Ortho- and para-iodoanisoïls have their iodine replaced by bromine when treated with that substance; the product in both cases is 2 : 4-dibromoanisoïl; the latter, when dissolved in cold, fuming nitric acid, yields a 2 : 4-*dibromonitroanisoïl*, $OMe{\cdot}C_6H_2Br_2{\cdot}NO_2$, which crystallises from dilute alcohol in long, silky, yellowish needles, and melts at 116—117°. If, before bromination, pariodoanisoïl be diluted with five times its weight of chloroform, the product is 2 : 4-*bromiodoanisoïl*, melting at 89°. Orthoiodoanisoïl, under similar conditions, yields 4 : 2-*bromiodoanisoïl*, melting at 68°; both substances form large, white, rhombic tables, and crystallise with great readiness.

*Metiodoanisoïl*, $OMe{\cdot}C_6H_4I$, is readily prepared from metiodophenol; it forms an oil, which is readily soluble in alcohol and ether, and has an odour recalling that of iodobenzene and not that of anisoïl; it boils at 244—245° (corr.); it is attacked by bromine with even greater energy than the corresponding ortho- and para-derivatives, but the iodine is not displaced; the product is a *bromiodoanisoïl*,

$$OMe{\cdot}C_6H_3BrI,$$

and forms an oil, which boils and decomposes at 285—295° at the ordinary pressure, but may be distilled without alteration in a vacuum, its boiling point then being 163—164°; it does not give a solid nitro-derivative, but when treated with chlorine and then reduced, it yields a *chlorobromiodoanisoïl*, $OMe{\cdot}C_6H_2ClBrI$, which separates from alcohol in snow-white crystals, melting at 111—112°. A. L.

**Rational Methods for preparing Iodoxy-Compounds.** By H. CONRAD C. WILLGERODT (*Ber.*, 1896, **29**, 1567—1575).—The method of preparing an aromatic idoxy-compound, $R{\cdot}IO_2$, by heating the corresponding iodoso-compound, $R{\cdot}IO$, is not satisfactory, because half of the latter goes back into the state of the iodo-compound, $R{\cdot}I$. The author has found that it is possible to obtain the iodoxy-compound by the use of an oxidising agent, and thus avoid this loss. Many methods were tried; the iodoso-compound was directly oxidised with "hypochlorous acid" (prepared by saturating bleaching powder solution with carbonic anhydride, and filtering), with bleaching powder solution, or with sodium hypochlorite (from bleaching powder and sodium carbonate); or the iododichloride, $R·ICl_2$, was oxidised with sodium hypochlorite, or with bleaching powder solution; or the iodo-compound was chlorinated in aqueous solution, sodium hydroxide added to the iododichloride so formed, and more chlorine passed in, or it was oxidised with "hypochlorous acid," or with sodium hypobromite. In all cases the iodoxy-compound was obtained, and in many of them the yield was quantitative. The method which, on the whole, the author seems to regard as the most trustworthy, is the oxidation of the iododichloride with bleaching powder solution. Iodoxybenzene, parachloriodoxybenzene, paraiodoxytoluene, and *β-iodoxynaphthalene* were prepared in this way. The last is a new substance; it detonates at 200° when pure; in its preparation β-iodophthalic acid was obtained as a bye-product. C. F. B.

**New Methods of Research in Organic Chemistry.** By WALTER LÖB (*Ber.*, 1896, **29**, 1390—1392).—Many reactions which occur under the influence of an electric current can be carried out in a convenient manner by so arranging the reacting substances that they make up a galvanic element. Thus when a porous cell filled with a solution of nitrobenzene in concentrated sulphuric acid is put into a solution of dilute sulphuric acid, a piece of platinum placed in the nitrobenzene solution, and a piece of zinc in the dilute sulphuric acid, and the two metals then connected, the nitrobenzene is rapidly and completely reduced to amidophenol. In a similar manner orthonitrobenzoic acid dissolved in an alkali may be reduced to azoxy- and hydrazo-benzoic acid. Many other reactions can be carried out in a similar way. A. H.

**Derivatives of Phenylic Ether.** By CARL HAEUSSERMANN and H. TEICHMANN (*Ber.*, 1896, **29**, 1446—1450).—*Para-* and *ortho-nitrophenylic ether*, $C_6H_5·O·C_6H_4·NO_2$, were prepared by heating the corresponding chloronitrobenzenes with potassium phenoxide and phenol at 150°. They yield hydrazo-compounds when reduced with zinc dust and alcoholic potash, and these are oxidised by a current of air, or by ferric chloride, into azo-compounds. When reduced with tin and alcoholic hydrogen chloride, paranitrophenyl ether yields an imido-ether. Potassium paranitrophenoxide does not react so readily; in order to get a dinitrophenyl ether, it has to be brought in small quantities into a large excess of 1 : 4-chloronitrobenzene kept at a temperature of 225—235°.

The following compounds were prepared; the numbers indicate melting points, except where otherwise stated. *Nitrophenylic ethers*: *para-*, 61°, boils at 320°; *ortho-*, boils at 205° under 45 mm. pressure, sp. gr. = 1·258 at 15°. *Parahydrazophenylic ether*, yellowish, 116° (impure). *Azophenylic ethers*: *para-*, orange, 149·5—150°; *ortho-*, red, 168—169°. *Paramidophenylic ether*, stable in air, 84° (*acetyl derivative*, 127°). *Diparanitrophenylic ether*, yellowish, 142·5—143°, probably identical with the substance obtained by Hoffmeister (*Annalen*, **159**, 207) in the nitration of phenyl ether. *Diparamidophenylic ether*, 186—187° (Hoffmeister, 185°); the *hydrochloride* crystallises with $H_2O$; yields azo-dyes that may possibly have a commercial value. A *orthoparadinitrophenylic ether*, $O(C_6H_4 \cdot NO_2)_2$, 103·5°, has also been obtained. C. F. B.

**Chemical Constitution and Oxidisability in presence of Laccases.** By Gabriel Bertrand (*Compt. rend.*, 1896, **122**, 1132—1133).—In the case of dihydric and trihydric phenols, amidophenols, and diamidobenzenes, the ortho- and para-derivatives are readily oxidised by oxygen or air in presence of laccase, whilst the meta-derivatives are not. Pyrocatechuic acid, gallic acid, and hexahydric phenol, $C_6(OH)_6$, are also readily oxidised. The rate of oxidation seems to depend on the tendency of the particular compound to form a quinone, and the general conclusion is that laccase acts most readily, if not exclusively, on compounds of the benzene series which contain not fewer than two hydroxyl or amidogen groups in the ortho- or para-position (compare Abstr., 1895, i, 386). C. H. B.

**Action of Ethylic Orthoformate on Primary Aromatic Amines.** By Reinhold Walther (*J. pr. Chem.*, 1896, [2], **53**, 472—478).—This paper contains the details of the work which has already been summarised in this vol., i, 165. A. G. B.

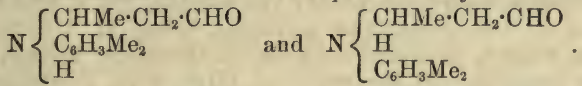
**Stereochemistry of Nitrogen Compounds.** By Wilhelm von Miller and Josef Plöchl [with G. Mozdzynski (*Ber.*, 1896, **29**, i, 1462—1472).—If xylidine $[Me_2 : NH_2 = 1:3:4]$ is dissolved in dilute hydrochloric acid, acetaldehyde added, and the mixture allowed to remain for 24 hours, condensation takes place, and a mixture of two isomeric substances, $C_6H_3Me_2 \cdot NH \cdot CHMe \cdot CH_2 \cdot CHO$, is eventually obtained. The one crystallises in long, triclinic prisms, melts at 131°, and is sparingly soluble in the ordinary solvents, the other crystallises in short, monoclinic prisms having the appearance of rhombohedra, melts at 102°, and is readily soluble. On crystallising the mixture, however, the substance of higher melting point first separates, and then a mixture of the two substances, from which that of lower melting point can only be isolated by picking out its crystals with the aid of a lens. Each substance yields a nitroso-derivative, and both yield the same *benzoyl* derivative; the latter melts at 157°, and from it the isomeride melting at 131° is regenerated. Further, both yield the same *oxime*, melting at 165°, and they also condense with aromatic amines, $NH_2R$, yielding compounds

$$C_6H_3Me_2 \cdot NH \cdot CHMe \cdot CH_2 \cdot CH \colon NR;$$

the aniline, anisidine, and 1 : 3 : 4 xylidine compounds melt at 95°, 118—119°, and 147° respectively; from the last compound, the substance of melting point 102° is regenerated when it is allowed to remain with hydrochloric acid. This compound is also the direct product of condensation when aldehyde and xylidine, suspended in much water, are warmed together at 70°. Yet another condensation product, melting at 55—60°, has been obtained, but it has not been investigated.

The two aldehyde bases are obviously stereoisomeric; they have different physical properties, but react chemically in the same way. As indicated above, the isomeride melting at 102° can be converted into the other by passage through the benzoyl derivative, and the reverse transformation can be effected by means of the xylidine derivative; the isomeride of lower melting point is also partly converted into the other, when it is recrystallised, warmed with water, heated above its melting point, &c. The isomerism cannot be due to the asymmetric carbon atom, for both substances are optically inactive. It is a *stereoisomerism of a new kind*, and must be regarded as due to the different arrangement, in one plane, of the groups united to the nitrogen atom.

The two substances are therefore represented by the formulæ



$$N\begin{cases} CHMe{\cdot}CH_2{\cdot}CHO \\ C_6H_3Me_2 \\ H \end{cases} \text{and} \quad N\begin{cases} CHMe{\cdot}CH_2{\cdot}CHO \\ H \\ C_6H_3Me_2 \end{cases}.$$

The first formula is assigned to the compound melting at 102°, because it readily yields a quinaldine when heated above its melting point or when boiled with hydrochloric acid, and must therefore contain the aldehyde group and the benzene ring in closer proximity than is the case with its isomeride, which yields hardly any quinaldine under similar circumstances. C. F. B.

**Thiodiphenylamine.** By OSKAR UNGER and KARL A. HOFMANN (*Ber.*, 1896, **29**, 1362—1368; compare Abstr., 1895, i, 132).—Thiodiphenylamine hydrochloride is deposited in colourless, slender needles when the amine, dissolved in alcohol, is saturated with hydrogen chloride and cooled to 0°. Mono-, di-, and tetra-chlorothiodiphenylamines are obtained together by dissolving the amine in anhydrous ether containing 3—4 per cent. of hydrogen chloride, and treating the well-cooled solution with the oxides of nitrogen evolved from arsenious anhydride and nitric acid (sp. gr. = 1·3); the amine may also be dissolved in ether, treated with nitric oxides, and the resulting product heated with alcoholic hydrogen chloride; the former method gives all three compounds, the latter chiefly the tetrachloro-derivative. The best yield of the mono- and dichloro-compounds is obtained by dissolving the amine (3 parts) in alcoholic hydrogen chloride, and adding sodium nitrite (1 part) dissolved in a little water, the temperature is maintained at 0° during about an hour, and finely divided copper is added. *Tetrachlorothiodiphenylamine*, $C_{12}H_5NSCl_4$, is sparingly soluble in alcohol; it is formed, together with the blue compound previously described (*loc. cit.*), by heating with aniline and aniline hydrochloride the substance formed by the action of nitric oxides on the amine in ethereal solution, and, in small quantity, by the action of chlorine on the amine in chloroform solution at 30°; it crystallises from benzene in pale yellow, slender needles melting at 235°. It is not changed by concentrated sulphuric acid at the ordinary temperature, but when warmed, a deep violet solution is obtained which has a well-defined absorption band, the maximum being at $\lambda = 596$. With concentrated nitric acid, the tetrachloramine evolves chlorine and yields a nitro-derivative, with nitric acid diluted with glacial acetic acid, an oxidation product, probably

$C_{12}H_5NSCl_4O$, is formed; this crystallises in red, lustrous prisms, and does not yield a dye when reduced. These reactions indicate that the chlorine occupies in both nuclei the positions 2 : 4. Mono- and di-chlorothiodiphenylamine are readily soluble in alcohol; when diluted and the product crystallised from benzene, greenish, silvery, lustrous plates are obtained which consist of an isomorphous mixture containing 2 mols. of the dichloro-compound : 5 mols. of the monochloride; the substances are separated by repeated crystallisation from benzene and alcohol. *Dichlorothiodiphenylamine*, $C_{12}H_7NSCl_2$, crystallises from alcohol in slender, colourless plates, of silvery lustre, melting and decomposing at 225—227°; it becomes green when exposed to air, and dissolves in concentrated sulphuric acid with an intense cherry-red colour; the solution has a broad absorption band in the green, the maximum being at $\lambda = 569$. The molecular weight, determined by the ebullioscopic method, agrees with the formula. By the action of nitric acid, *dinitrodichlorodiphenylsulphoxide*, $C_{12}H_5(NO_2)_2NCl_2SO$, is formed; it crystallises in yellow needles, and, when reduced by means of stannous chloride and hydrochloric acid, yields leucoisothionine; the nitro-groups, and therefore also the chlorine atoms, probably occupy the positions 2 : 4, NH = 1. An isomeric *dichlorothiodiphenylamine* is obtained in very small quantity, together with the tetrachloro-compound, by the direct action of chlorine on the amine; it crystallises in pale, grass-green prisms, melts at 222°, and when nitrated and reduced, yields no dye, indicating that both chlorine atoms are in the para-position. *Chlorothiodiphenylamine*, $C_{12}H_8NSCl$, could not be completely purified; in general properties it closely resembles the dichloro-derivative, its characteristic absorption band attains a maximum at $\lambda = 544$. The compounds formed by the action of hydrogen chloride and nitric oxides respectively on thiodiphenylamine (see above) are amorphous and too unstable to purify; the former evolves 60—70 per cent. of its chlorine as hydrogen chloride when it is heated at 100°, the ratio N : S : Cl = 1 : 1 : 1·2; the nitric oxides appear to act as dehydrating agents, no nitrosamine or nitroso-derivative is formed, and all attempts to prepare the latter were fruitless. The action of hydrogen chloride on thiodiphenylamine and on quinone appear to be similar; in the latter case also an additive compound is formed and an intense coloration produced. J. B. T.

**Action of Aldehydes on Aromatic Orthodiamines. IV.** By Oscar Hinsberg and P. Koller (*Ber.*, 1896, **29**, 1497—1504).—The condensation between aldehydes and aromatic orthodiamines appears to be of a general character. Compounds of the formulæ

$$H_2N\cdot C_xH_y\cdot N\colon CHR \text{ and } C_xH_y(N\colon CHR)_2$$

being formed. The compounds produced by the condensation of ethylic acetoacetate and aromatic orthodiamines appear to have an analogous structure.

*Benzylideneorthophenylenediamine*, $H_2N\cdot C_6H_4\cdot N\colon CHPh$, formed by the condensation of orthophenylenediamine with benzaldehyde (1 mol.), is a yellow, crystalline solid melting at 60—61°, after recrystallisation from light petroleum (40—50°). It is readily converted into the imidazole melting at 280° by either heating alone at 100°, or by boiling its alcoholic or ethereal solution in the air; benzylideneorthophenylenediamine is in its mode of preparation and properties closely analogous to paranitrobenzylideneorthophenylenediamine (Hinsberg and Funcke, Abstr., 1894, i, 623).

*Dibenzylideneorthophenylenediamine*, $C_6H_4(N{:}CHPh)_2$, is formed when 2 mols. of benzaldehyde react with 1 mol. of orthophenylenediamine. It crystallises from light petroleum in yellow prisms melting at 106°, and it is soluble in alcohol, ether, and light petroleum, insoluble in water. By heating with dilute mineral acids, it is split up into benzaldehyde and orthophenylenediamine.

*Benzylidene*-1 : 2-*naphthylenediamine*, $NH_2\cdot C_{10}H_6\cdot N{:}CHPh$, prepared from 1 : 2-naphthylenediamine and benzaldehyde (1 mol.) forms yellow crystals melting at 156—157°. It is very stable, and remains unaltered on passing air through its boiling alcoholic solution. It, however, yields a derivative of the imidazole series (m. p. 210°) when dissolved in a solution of bromine in sodium hydroxide. Whether the N:C group is in the α- or β-position has not yet been determined. The corresponding dibenzylidene compound is not formed when 2 mols. of benzaldehyde react with 1 mol. of 1 : 2-naphthylenediamine in the cold; on warming, an imidazole base is produced.

*Ethylic amidophenylimido-β-butyrate*,

$$NH_2\cdot C_6H_4\cdot N{:}CMe\cdot CH_2\cdot COOEt,$$

is produced by shaking finely divided orthophenylenediamine with an equivalent quantity of ethylic acetoacetate, and is purified by recrystallisation from light petroleum; it melts at 85°. An isomeric compound melting at 59° is also produced in this reaction; by repeated recrystallisation from light petroleum it passes into the substance melting at 85°. It is probably a substituted amidocrotonic acid, $NH_2\cdot C_6H_4\cdot NH\cdot CMe{:}CH\cdot COOEt$.

*Ethylic paranitrobenzylideneamidophenylimido-β-butyrate*,

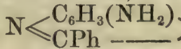
$$NO_2\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot N{:}CMe\cdot CH_2\cdot COOEt,$$

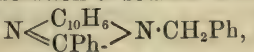
prepared from ethylic amidophenylimidobutyrate and paranitrobenzaldehyde (1 mol.) melts at 99°; it is decomposed by long boiling of its alcoholic solution.

*Methylic orthamidophenylimidobutyrate*,

$$NH_2\cdot C_6H_4\cdot N{:}CMe\cdot CH_2\cdot COOMe,$$

produced in the same way as the ethylic salt, crystallises from light petroleum in white needles melting at 87°.

*Amidobenzaldehydine*,  $N{<}\begin{matrix}C_6H_3(NH_2)\\ CPh\text{———}\end{matrix}{>}N\cdot CH_2Ph$, melts at 121°, and is obtained from 1 : 2 : 4-triamidobenzene and 2 mols. of benzaldehyde. It can be purified by dissolving in alcohol and precipitating by means of a concentrated solution of sodium chloride.

*αβ-Naphtobenzaldehydine*,  $N{<}\begin{matrix}C_{10}H_6\\ CPh\text{-}\end{matrix}{>}N\cdot CH_2Ph$, melts at 117°, and is formed by adding benzaldehyde to an acetic acid solution of 1 : 2-naphthylenediamine hydrochloride. J. F. T.

**Bromine Derivatives of Metaphenylenediamine.** By C. LORING JACKSON and SIDNEY CALVERT (*Amer. Chem. J.*, 1896, **18**, 465—489).—*Tribromometaphenylenediamine* is prepared by passing a stream of air laden with bromine vapour into a solution of metaphenylenediamine, an excess of bromine being avoided. The precipitate is crystallised from alcohol, and assumes the form of long, slender, white, silky needles united longitudinally into ribbons with serrated ends. It melts at 158°, and dissolves freely in hot alcohol, ether, benzene, chloroform, glacial acetic acid, and carbon bisulphide, very slightly in light petroleum, and not in water. The diamine is a feeble base, but its *hydrochloride* was prepared by passing hydrogen chloride into a benzene solution of the base. By treating the diamine in benzene solution with acetic chloride, the *diacetamide*,

$$C_6HBr_3(NHAc)_2,$$

was prepared; it crystallises from hot glacial acetic acid in aggregates of small, white plates; it does not melt at 330°, and is very slightly soluble in all common solvents. *Tribromophenylenediurethane*, $C_6HBr_3(NH{\cdot}COOEt)_2$, was prepared by boiling the diamine with ethylic chlorocarbonate; it crystallises in white needles, melts at 212°, and dissolves freely in hot alcohol, hot benzene, chloroform, and acetone, but not in light petroleum.

When tribromodinitrobenzene (m. p. 192°, made from symmetrical tribromobenzene) is reduced by zinc dust and acetic acid, it yields tribromophenylenediamine; but when the reduction is effected by tin and hydrochloric acid, all three bromine atoms are removed, metaphenylenediamine being produced. It was found that tribromophenylenediamine also parts with all its bromine when treated with tin and hydrochloric acid, but symmetrical tribromobenzene was unaltered by this treatment, although tribromaniline parted with a bromine atom in the ortho-position to the amido-group under the same conditions.

Metaphenylenediamine yields a tribromo-derivative when brominated, but metaphenylenediacetamide gives only *dibromometaphenylenediacetamide* when brominated in acetic acid solution, even though the bromine be in considerable excess. This compound crystallises in small, short prisms, melts and decomposes at 259—260°, and dissolves sparingly in alcohol, freely in benzene, chloroform, and glacial acetic acid, but not at all in ether and light petroleum. By hydrolysing the diacetamide with strong hydrochloric acid, a *dibromometaphenylenediamine* is obtained; it crystallises in white, slender needles, melts at 135°, and dissolves freely in alcohol, acetone, ether, hot chloroform and hot benzene, but only slightly in light petroleum and water; it forms salts more easily than the tribromo-derivative does, but is more difficultly debrominated; the *hydrochloride* and the *hydrobromide* are described.

The reduction of tetrabromodinitrobenzene by tin and hydrochloric acid in alcoholic solution yields *bromometaphenylenediamine* (? symmetrical), which crystallises in needles and monoclinic prisms, melts at 93—94°, and dissolves freely in acetone, alcohol, ether, and chloroform, slightly in benzene and carbon bisulphide, moderately in water, and hardly at all in light petroleum; the *hydrobromide* is described. By bromination in ether, it yields *tetrabromometaphenylenediamine*, which crystallises in small, white needles, melts at 212—213°, and dissolves freely in benzene, chloroform, ether, acetone, carbon bisulphide, and hot alcohol, but very slightly in light petroleum; its basic properties are very feeble. A. G. B.

**Oxidation Products of Orthamidodiphenylamine [Phenylorthophenylenediamine].** By OTTO FISCHER and A. DISCHINGER (*Ber.*, 1896, **29**, 1602—1608; compare Abstr., 1893, i, 266).—In order to meet the criticism of Kehrmann (Abstr., 1895, i, 527), the authors have repeated the experiments of Fischer and Heiler on the oxidation of phenylorthophenylenediamine by means of ferric chloride (Abstr., 1893, i, 266), and have confirmed their results. The chief product of the oxidation is anilidoaposafranine, which melts at 203—204°, and is identical with the compound prepared from aposafranine and aniline. When treated with alkalis, it yields anilidoaposafronone and hydroxyaposafranone, as found by Fischer and Heiler. This proves that the formula proposed by these chemists for anilidoaposafranine is the correct one. The anilidoaposafranine is accompanied by a second substance which probably has the composition $C_{36}H_{27}N_5$, and melts at 258—259°. This compound is probably formed by a secondary reaction between the anilidoaposafranine and phenylorthophenylenediamine. The presence of a small amount of this substance in the product obtained by Fischer and Heiler was the cause of the high melting point which these chemists ascribed to anilidoaposafranine.

NOTE BY OTTO FISCHER AND EDUARD HEPP.—The formation of phenylfluorindine both from the oxidation product of phenylorthophenylenediamine and the anilidoaposafranine obtained synthetically, is a further proof of the accuracy of the formula proposed by Fischer and Heiler for the latter compound. Phenylfluorindine can be crystallised without change from ethylic benzoate if the solution be only boiled for a moment or two and then rapidly filtered (compare Kehrmann and Bürgin, this vol., i, 512). A. H.

**Symmetrical Triamidotoluene.** By ARTHUR W. PALMER and WILLIAM C. BRENKE (*Ber.*, 1896, **29**, 1346—1347).—Trinitrodibromotoluene (m. p. 229°) is slowly reduced by means of tin and hydrochloric acid; after purification, the resulting *triamidotoluene* is colourless and crystalline; the *hydrochloride*, $C_6H_2Me(NH_2)_3,3HCl$, crystallises in various forms, depending on the temperature and concentration of the solution. The *sulphate* and *picrate* are also crystalline, the former being deposited in short prisms. J. B. T.

**Composition of the Isodiazohydroxides.** By EUGEN BAMBERGER (*Ber.*, 1896, **29**, 1383—1388; compare this vol., i, 246).—The author has succeeded in analysing paranitroisodiazobenzene hydroxide and its sodium and silver salts, as well as *primary potassium isodiazobenzenesulphonate*, $SO_3K\cdot C_6H_4\cdot N_2\cdot OH + H_2O$. The latter is a lustrous, crystalline precipitate, and is obtained by adding acetic acid to the dipotassium salt. The *disilver salt*, which has also been analysed, is a crystalline powder which is decomposed by hot water. The hydroxides of isodiazobenzene and isodiazoparatoluene were found to be too unstable for analysis. The *potassium salt* of the latter forms silver-white, nacreous plates.

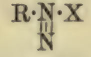
*Phenyl*-a-*paranitrophenyl*-h-*phenylmethylformazyl*,

$$NO_2\cdot C_6H_4\cdot N_2\cdot CPh{:}N\cdot NMePh,$$

is obtained by the action of paranitroisodiazobenzene hydroxide on benzylidenephenylmethylhydrazine in alcoholic solution at −5°. It crystallises in brownish-red needles, which have a bronze lustre, and melt at 201—202°; its solution in concentrated sulphuric acid has a deep violet-red colour. This is the first instance of the formation of a formazyl compound by the action of a diazo-compound on a secondary hydrazone. A. H.

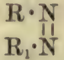
[**Normal Diazo-metallic Salts.**] By EUGEN BAMBERGER (*Ber.*, 1896, **29**, 1388—1390).—The author again maintains the experimental accuracy of his criticism of the results published by Hantzsch (this vol., i, 428). A. H.

**Diazophenols.** By ARTHUR R. HANTZSCH and WILLIAM B. DAVIDSON (*Ber.*, 1896, **29**, 1522—1534).—The following arguments are put forward in order to show under which of the three types



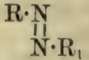
$$\begin{array}{l}R\cdot N\cdot X\\ \quad\ \ |||\\ \quad\ \ N\end{array}$$

Diazonium salt.



$$\begin{array}{l}R\cdot N\\ \quad\ \ ||\\ R_1\cdot N\end{array}$$

Syndiazo-compound.



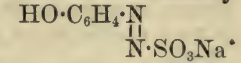
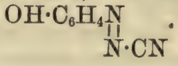
$$\begin{array}{l}R\cdot N\\ \quad\ \ ||\\ \quad\ \ N\cdot R_1\end{array}$$

Antidiazo-compound.

the diazophenols and their salts, the salts of paradiazophenolsulphonic acid, and paradiazophenol cyanide should be placed.

The diazophenols behave as the internal anhydrides of very weak bases; they are now found to have a very low electrical conductivity, and, since their cryoscopic behaviour corresponds with a simple molecular weight, this would speak in favour of their being syndiazo-anhydrides; this argument is, however, weakened from the fact that the trimethylamidophenols, which can only be inner ammonium anhydrides, show identical behaviour.

Other considerations, notably the fact that the oxydiazonium ion, $HO\cdot C_6H_4\cdot N{:}N$, is colourless and insoluble in organic solvents not containing hydroxyl, as are also the anhydrides of the trimethylamidophenols, whilst the ring diazo-compounds are coloured and soluble in organic solvents, points to their being in reality syndiazo-anhydrides, $R{<}\genfrac{}{}{0pt}{}{N}{O}{>}N$. The non-substituted diazophenols appear to exist in both forms simultaneously, $C_6H_4{<}\genfrac{}{}{0pt}{}{N}{O}{>}N \rightleftarrows C_6H_4{<}\genfrac{}{}{0pt}{}{N{:}N.}{|\atop O}$

With regard to the salts of the diazophenols, there can be no doubt as to their being pure oxydiazonium salts. Diazophenol chloride is therefore oxydiazonium chloride, $HO\cdot C_6H_4\cdot N_2\cdot Cl$. The salts of diazophenolsulphonic acids are, from their stability and their inability to unite with phenols, antidiazo-compounds,  $\begin{array}{l}HO\cdot C_6H_4\cdot N\\ \quad\quad\quad\|\\ \quad\quad N\cdot SO_3Na\end{array}$. Similarly diazophenol cyanide, $OH\cdot C_6H_4\cdot N_2\cdot CN$, is stable, and does not combine with phenols; it is therefore probably  $\begin{array}{l}OH\cdot C_6H_4N\\ \quad\quad\quad\|\\ \quad\quad N\cdot CN\end{array}$. The corresponding acid has been obtained.

Free *paradiazophenol*, $C_6H_4N_2O + 4H_2O$, prepared by the action of moist silver oxide on paradiazophenol chloride, forms yellow needles, melting at 38—39°; it loses water gradually over sulphuric acid, but then decomposes rapidly, especially in the light. Its intensely yellow aqueous solution is only decomposed slowly on boiling; with cadmium iodide, it forms a well-defined crystalline compound, $C_6H_4N_2O + CdI_2$.

Free *orthodiazophenol* could not be obtained in the solid state. The *meta*-compound is so unstable that its chloride decomposes in aqueous solutions at 0°.

The following double salts have been isolated.

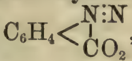
$OH\cdot C_6H_4\cdot N_2Cl,HgCl_2 + H_2O$ [HO : NNCl = 1 : 4], white needles, decomposing at 156°.

$OH\cdot C_6H_4\cdot N_2I,HgI_2$ [HO : NNI = 1 : 4] is unstable, and melts at 110°.

$OH\cdot C_6H_4\cdot N_2I,HgI_2 + C_6H_4N_2O$ is stable, and melts at 132°. The similar compound with cadmium iodide melts at 134°.

*Antiparadiazophenol cyanide*, $OH\cdot C_6H_4\cdot N{:}N\cdot CN$, prepared from paradiazophenol chloride and potassium cyanide, forms yellow needles which explode at 117°.

*Potassium antidiazophenolcarboxylate*, $OK\cdot C_6H_4\cdot N{:}N\cdot COOK$, is formed from this cyanide by the action of alcoholic potash; it is very unstable.

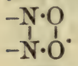
The authors conclude with a comparison between the diazo- and the trimethylamido-phenols, and finally describe free *diazoanthranilic acid*,  $C_6H_4<\begin{array}{c}N{:}N\\ |\\ CO_2\end{array}$, or, more correctly, *diazoniumanthranilic acid*. It is made by diazotising anthranilic acid, and is very unstable, exploding violently when rubbed, whilst its aqueous solution decomposes slowly, with the formation of salicylic acid. J. F. T.

**Action of Benzene Sulphonic Chloride on Nitrosodimethylaniline.** By ERNST BÖRNSTEIN (*Ber.*, 1896, **29**, 1479—1488).—By acting on nitrosodimethylaniline with benzenesulphonic chloride in benzene solution, at ordinary temperatures, the following substances were isolated.

*Tetramethylazoxyaniline*, $ON_2(C_6H_4\cdot NMe_2)_2$, is obtained by shaking the benzene solution after the reaction, with dilute sulphuric acid, precipitating the acid solution with sodium carbonate, and washing thoroughly with water; it melts at 244·5°, and forms small, brown crystals.

After the extraction with sulphuric acid, the benzene solution is evaporated to dryness and treated with cold absolute alcohol, when it yields a soluble and an insoluble product.

The latter melts at 183° and crystallises from hot alcohol in yellow plates; it appears to be an azo-peroxide, formed by the condensation of two molecules of nitrosodimethylaniline, and containing the group



$$\begin{array}{l} -N\cdot O \\ \;\;\, | \quad | \\ -N\cdot O \end{array}.$$

The portion soluble in alcohol, on evaporation, yields a brown, crystalline mass, from which, on recrystallisation from methylic alcohol, cinnabar-red crystals of *trimethylazoxyaniline*,

$$NHMe\cdot C_6H_4\cdot N_2O\cdot C_6H_4\cdot NMe_2,$$

melting at 144°, are obtained; this is interesting from the fact that it is the only asymmetrical azoxy-compound known.

*Paranitrosophenylic benzenesulphonate*, $Ph\cdot SO_3\cdot C_6H_4\cdot NO$, is also found in the benzene solution after treatment with sulphuric acid; it melts at 132°, and forms long, light yellow prisms from dilute alcohol. J. F. T.

**Reduction by means of Phenylhydrazine.** By REINHOLD WALTHER (*J. pr. Chem.*, 1896, [2], **53**, 433—471; compare Abstr., 1895, i, 595).—Details of the processes requisite for the reduction of nitrobenzene to aniline, of nitrotoluenes to the corresponding toluidines, of metadinitrobenzene to metanitraniline, of orthonitraniline to orthophenylenediamine, of orthonitrophenol to orthamidophenol, of paranitrophenol to paramidophenol, and of orthonitrobenzoic acid to orthamidobenzoic acid, by means of phenylhydrazine are given; except in the last three cases, the nitro-compound is heated with three molecular proportions of phenylhydrazine at first at atmospheric pressure and finally in an autoclave, xylene being used as a diluent when the action is violent. The acid character of the nitrophenols and of the nitrobenzoic acid entails the use of a larger proportion of phenylhydrazine than that given above. The action of phenylhydrazine on azoxybenzene, and on phenylhydroxylamine is very energetic, aniline being among the products. Nitromethane and nitroethane are attacked with difficulty by phenylhydrazine; ethylic nitrate reacts explosively. For the behaviour of phenylhydrazine towards nitroso-compounds consult O. Fischer and Wacker (Abstr., 1888, 1286; 1889, 702) whose work is here confirmed. Bamberger's diazohydroxyamidobenzene (this vol., i, 222) was obtained from nitrosobenzene and phenylhydrazine.

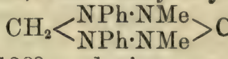
Attempts to obtain symmetrical phenylmethylhydrazine by the reduction of formylphenylhydrazine by phenylhydrazine failed. Neither the group C⁚N, as it occurs in the hydrazones, nor the group C⁚C can be reduced by phenylhydrazine.

The nitrobenzylidenephenyldrazones have been prepared by Pickel (Abstr., 1886, 545) and by Lepetit (Abstr., 1887, 845). The *benzoyl*- and *acetyl* derivatives of the meta-compound are colourless, and melt at 197° and 170° respectively; the *benzoyl* and *acetyl* derivatives of the para-compound are also colourless and melt at 169° and 160—162° respectively; *benzoylorthonitrobenzylidenephenylhydrazone* crystallises in yellow prisms, and melts at 166—167°. The nitro-compounds are readily reduced by phenylhydrazine when heated therewith under pressure; *metamidobenzylidenephenylhydrazone* crystallises in light yellow needles and melts at 162°; the *para*-derivative in golden-yellow laminæ, melting at 175°; and the *ortho*-derivative in greenish-yellow laminæ, melting at 221—222°.

The foregoing benzoyl and acetyl derivatives were conveniently prepared by treatment of the hydrazone with the acid chloride in a pyridine solution and subsequent addition of water. The same method served for the preparation of benzoylbenzylidenephenylhydrazone which was found to melt at 114° (compare Abstr., 1887, 820).

Azobenzene was readily reduced to hydrazobenzene when heated with phenylhydrazine and the product was free from the camphor odour usually ascribed to it; by the further action of phenylhydrazine, aniline and benzene were formed. Amidoazobenzene is similarly reduced to paraphenylenediamine, aniline, benzene, and nitrogen. Diazoamidobenzene (best purified by recrystallisation from alcohol, not from light petroleum as commonly stated) yielded aniline, benzene, and nitrogen. By heating thiocarbanilide and phenylhydrazine in alcohol, diphenylthiosemicarbazide may be obtained; this undergoes a further change, not yet defined, when heated under pressure with phenylhydrazine. The behaviour of amidines with phenylhydrazine is briefly described and it is pointed out that phenylhydrazine undergoes self reduction to aniline, benzene, nitrogen, and ammonia when heated in an autoclave at 300°.

A. G. B.

**Action of Formaldehyde on Phenylhydrazine in Acid Solution.** By CARL GOLDSCHMIDT (*Ber.*, 1896, **29**, 1361—1362).—The compound $CH_2(NPh{\cdot}N{:}CH_2)_2$ is formed by the action of phenylhydrazine hydrochloride and methylenedimethyl ether in presence of hydrochloric acid at the ordinary temperature; it is deposited in pale yellow crystals, and melts at 112°; the molecular weight was determined by the cryoscopic method. The presence of phenylhydrazine in excess favours the formation of the compound, but it could not always be successfully prepared. When gently heated with phenylhydrazine in presence of hydrochloric acid, formaldehyde yields a compound which possibly has the formula  $CH_2{<}\begin{matrix}NPh{\cdot}NMe\\NPh{\cdot}NMe\end{matrix}{>}CO$; it crystallises in rhombic plates, melts at 128°, and gives a reddish-violet coloration with ferric chloride and hydrochloric acid. It is completely decomposed by heating with concentrated hydrochloric acid. The *hydrochloride*, formed in ethereal solution, is unstable.

J. B. T.

**Action of Formaldehyde on *as*-Phenylmethylhydrazine in Acid Solution.** By CARL GOLDSCHMIDT (*Ber.*, 1896, **29**, 1473).—Unsymmetrical phenylmethylhydrazine in hydrochloric acid solution gives a green colour with formaldehyde when allowed to remain for half an hour, or at once on warming in the water bath. No other aldehydes give this reaction, which may, therefore, be used as a test for formaldehyde. From the greenish, creamy mixture, ether extracts a yellowish-white substance melting at 217°, possibly with the constitution $CH_2(C_6H_4{\cdot}NMe{\cdot}N{:}CH_2)_2$. This colours silk and wool bluish-green; from its alcoholic solution sodium hydroxide precipitates the colour-base as a yellowish-brown substance. C. F. B.

**Symmetrical Carbamides of the Benzene Series.** By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1896, **122**, 1130—1131).—When boiled with aniline, guaiacol carbonate readily yields symmetrical diphenylcarbamide, identical with that obtained by the action of carbonyl chloride on aniline. It crystallises in needles which melt at 234—235°, and sublimes at 245°; it is only slightly soluble in cold alcohol and ether, more soluble in boiling alcohol, insoluble in chloroform and benzene. Previous descriptions of the physical properties of this compound seem to be incorrect.

*Diparatolylcarbamide*, obtained in a similar manner from paratoluidine, forms white crystals which melt at 244—245° and volatilise at the same temperature without decomposing. It is insoluble in most solvents, but can be crystallised from boiling alcohol.

*Diorthotolylcarbamide* separates from boiling alcohol in magnificent, white, silky crystals, which melt and sublime at 219—220°. It is very slightly soluble in most solvents.

All these substituted carbamides dissolve in concentrated sulphuric acid, and are precipitated unchanged on addition of water. If, however, they are heated with the acid above 115°, they are converted into sulphonic acids, with evolution of carbonic anhydride.

C. H. B.

**Halogen Derivatives of Fatty Amines.** By A. LUCHMANN (*Ber.*, 1896, **29**, 1420—1433).—*Ethylic α-phenoxybutyrate*,

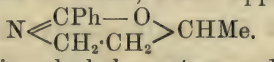
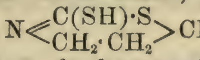
$$OPh{\cdot}CHEt{\cdot}COOEt,$$

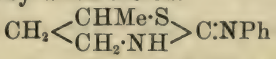
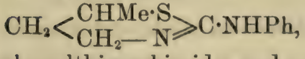
the product of the action of sodium phenoxide on ethylic α-bromobutyrate at 125—130°, distils at 250—251° at 748 mm. pressure; sp. gr. = 1·0388 at 24·5°; it has a faintly aromatic odour, and is insoluble in water, but miscible with alcohol and ether. *α-Phenoxybutyric* acid, OPh·Et·CH·COOH, is somewhat soluble in hot water, but not in cold, dissolves readily in alcohol and ether, but is only sparingly soluble in petroleum; it forms long odourless, colourless, shining needles, melts at 96—99°, and cannot be distilled without decomposing, but may be volatilised in steam; at 180° it is decomposed with liberation of phenol. The *silver* salt, $C_{10}H_{11}O_3Ag$, melts and decomposes at 202°; the *chloride* is instantaneously decomposed by water, and cannot be distilled without decomposing even under very low pressure (20 mm.). The *amide* dissolves readily in the ordinary media, crystallises in long needles, melts at 111°, and is slightly volatile even at 100°.

*α-Phenoxybutyronitrile*, OPh·CHEt·CN, is obtained in satisfactory amount when the amide is distilled with phosphorus pentachloride; it forms a colourless oil, insoluble in water, and boiling at 228—230° under 148 mm. pressure; unlike phenoxyacetonitrile, it is not reduced to an amide when treated in alcoholic solution with metallic sodium, being merely hydrolysed by this treatment. *α-Phenoxybutyrothiamide*, $OPh{\cdot}CHEt{\cdot}CSNH_2$, is soluble in alcohol, but is insoluble both in ether and in cold water; it crystallises from hot water in beautiful, shining needles, volatilises slightly at 100°, and melts at 127°, and is not reduced by sodium and absolute alcohol.

An attempt to prepare $\beta$-phenoxypropionic acid by the interaction of $\beta$-iodopropionic acid and sodium phenoxide failed, the product consisting entirely of an unsaturated compound of low boiling point (90—100°), probably phenylic acrylate.

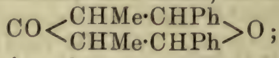
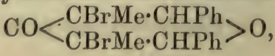
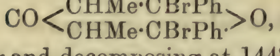
$\beta$-Ethoxybutyronitrile is readily reduced in alcoholic solution by means of sodium, yielding $\gamma$-ethoxybutylamine (Bookmann, this vol., i, 200); its sp. gr. = 0·8468 at 19°.

$\gamma$-Ethoxybutylamine and phenylthiocarbimide unite to form *$s\gamma$-ethoxybutylphenylthiocarbamide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}OEt$, which crystallises from absolute alcohol in large, colourless needles, melting at 91·5°. $\gamma$-Chlorobutylamine is formed when $\gamma$-ethoxybutylamine is heated, in sealed tubes, with fuming hydrochloric acid at 150°; it is only slightly volatile, and has a strong basic odour; the *hydrochloride* forms a brownish hygroscopic mass of crystals; the *platinochloride*, $(C_4H_8Cl{\cdot}NH_2)_2,H_2PtCl_6$, crystallises from hot water in golden-yellow leaflets, is readily soluble in alcohol, and melts and decomposes at 212°; the *picrate*, $C_4H_8ClNH_2,C_6H_3N_3O_7$, is readily soluble in water and alcohol, and crystallises from the former in yellow, rhombic tables; it melts at 144—146·5°, and at 200° decomposes, evolving gases. The *benzoyl* derivative forms an oil which solidifies in a freezing mixture, and is decomposed by alkali at 100°, yielding an oil volatile in steam, which appears to be 2 : 4-*phenylmethylpentoxazoline*,  $N{<}\begin{matrix}CPh—O\\CH_2{\cdot}CH_2\end{matrix}{>}CHMe$. The latter dissolves somewhat readily in alcohol, water, and ether, and has the characteristic odour of the oxazolines. Its *picrate*, $C_{11}H_{13}ON,C_6H_3N_3O_7$, forms slender, yellow needles, is sparingly soluble in water and alcohol, sinters at 141°, and melts at 146—148°; at 220° it begins to decompose. $\gamma$-Chlorobutylamine and carbon bisulphide unite in presence of alkali, and yield 4-*methylpenthiazoline 2-hydrosulphide*,  $N{<}\begin{matrix}C(SH){\cdot}S\\CH_2{\cdot}CH_2\end{matrix}{>}CHMe$; this crystallises from hot water in beautiful, long, feathery needles, dissolves readily in alcohol, chloroform, benzene, and alkalis, sparingly in ether and hot water, and is insoluble in acids; it sinters at 128°, and melts at 131°. The *ethosulphide*, $C_5H_8NS{\cdot}SEt$, is a clear, colourless liquid with a disagreeable odour of mercaptan, which boils at 256° under 754 mm. pressure, and dissolves readily in acids; its *platinochloride*, $(C_7H_{13}NS_2)_2,H_2PtCl_6$, crystallises from warm water in four-sided rhombic tables, and melts and decomposes at 151°; the *picrate* and the *dichromate* are oils, and do not solidify when cooled.

n-*Phenylbutylene-$\psi$-thiocarbamide*,  $CH_2{<}\begin{matrix}CHMe{\cdot}S\\CH_2{\cdot}NH\end{matrix}{>}C{:}NPh$ or  $CH_2{<}\begin{matrix}CHMe{\cdot}S\\CH_2—N\end{matrix}{\gg}C{\cdot}NHPh$, is the product of the interaction of phenylthiocarbimide and $\gamma$-chlorobutylamine in presence of alkali. It crystallises from dilute alcohol in long needles, softens at 104°, melts at 106·5°, and dissolves in alcohol, ether, and acids, but is insoluble in water; the *picrate*, $C_{11}H_{14}NS,C_6H_3N_3O_7$, crystallises from hot water in yellow needles, melts at 158—164°, and decomposes at 230°. γ-Chlorobutylamine and allylthiocarbimide yield n-*allylbutylene-ψ-thiocarbamide*, $C_8H_{14}N_2S$; this forms an oil which does not solidify at low temperatures; the *picrate*, $C_8H_{14}N_2S,C_6H_3N_3O_7$, crystallises from hot water in long needles, softens at 119° and melts at 121—122°, commencing to decompose at about 220°.

*Isocrotylamine* ($CH_2\!:\!CH\cdot CH_2\cdot CH_2\cdot NH_2$?) is produced when dilute alcoholic potash acts on γ-chlorobutylamine during five hours at 180°. The free base is very volatile, fumes in the air, and has a powerful odour reminiscent of allylamine; it boils at 80—90°. The *hydrochloride* unites with bromine, and appears to yield γ-chlorobutylamine when its solution is evaporated in presence of free hydrochloric acid. The *platinochloride*, $(C_4H_7\cdot NH_2)_2,H_2PtCl_6$, dissolves readily in hot water, less readily in cold water and alcohol; it crystallises from saturated alcoholic solutions in well-formed, golden-yellow, six-sided tables or prisms, which melt at 204°. The action of phenylthiocarbimide on the free base affords *phenylisocrotyl(?)thiocarbamide*, $NHPh\cdot CS\cdot NH\cdot C_4H_7$; this crystallises from dilute alcohol in slender needles, which melt at 94—97°. The properties of the foregoing compounds are not sufficiently distinct from those of derivatives of crotylamine (compare Schindler, Abstr., 1892, 32) to establish their non-identity with the latter; it is probable, however, that Schindler's base is identical with that obtained by Bookmann (*loc. cit.*) from β-chlorobutylamine. A. L.

**Benzimidoethyl and Benzimidomethyl Ethers.** By FRANK W. BUSHONG (*Amer. Chem. J.*, 1896, **18**, 490—491).—*Benzimidoethyl ether*, $C_6H_5\cdot C(NH)\cdot OEt$, was prepared by passing dry hydrogen chloride into benzonitrile and alcohol; the crystalline hydrogen chloride additive product was decomposed by caustic soda, and the new ether extracted by ether; it boils at 218°. Benzimidomethyl ether (Abstr., 1895, i, 522) was analogously prepared; it boils at 206°. Both ethers are colourless, mobile liquids with a pleasant odour; neither is solid at −30°. A. G. B.

**Action of Benzaldehyde on Diethyl Ketone.** By DANIEL VORLÄNDER and KARL HOBOHM (*Ber.*, 1896, **29**, 1352—1353; compare Abstr., 1894, i, 527).—Benzaldehyde (2 mols.) and diethyl ketone (1 mol.) combine in presence of alcohol and alkali, forming *diphenyldimethyltetrahydro-γ-pyrone*,  $CO<\substack{CHMe\cdot CHPh\\ CHMe\cdot CHPh}>O$; it is also obtained in small quantity during the preparation of benzylidenediethyl ketone. It is crystalline, melts at 106°, boils at 235—237° (20 mm.), and slowly solidifies. Acetic anhydride is without action on the compound. The *dibromo*-derivative,  $CO<\substack{CBrMe\cdot CHPh\\ CBrMe\cdot CHPh}>O$, or  $CO<\substack{CHMe\cdot CBrPh\\ CHMe\cdot CBrPh}>O$, crystallises in lustrous, white plates, melting and decomposing at 144°. Diethyl ketone differs from acetone in its behaviour towards benzaldehyde, since Claisen readily obtained dibenzylideneacetone. The formation of the pyrone is probably preceded by that of the ketoglycol $CO(CHMe\cdot CPh\cdot OH)_2$.

J. B. T.

**Diacetylmesitylene.** By VICTOR MEYER (*Ber.*, 1896, **29**, 1413—1414).—When mesitylene and acetic chloride, dissolved in carbon bisulphide, are warmed in presence of aluminium chloride, diacetylmesitylene is formed; it is also produced when acetylmesitylene is treated in a similar manner. It crystallises from light petroleum in white prisms, melts at 46°, and boils at 310° (corr.).

So far only durene, isodurene, and mesitylene have afforded diacetyl derivatives by this reaction, in all these substances, the acetyl group must of necessity assume the ortho-position with regard to two methyl groups.

Diacetylmesitylene, although it is a methylated 1 : 5-diketone, does not appear to undergo the characteristic condensation of this class of compounds, namely, the production of a six-carbon ring with elimination of water. This fact is of interest as evincing the greater rigidity of the benzene nucleus as compared with those of aliphatic compounds. A. L.

**Chemistry of Etherification.** By VICTOR MEYER (*Ber.*, 1896, **29**, 1397—1402).—(I) The author, in conjunction with C. SOHN, has obtained a small amount of prehnitylic acid, by the hydrolysis of the ethereal salt formed by the action of alcoholic hydrogen chloride on crude mesitylenic acid prepared from acetone. This appears to confirm the observations of Lucas, from which he concluded that mesitylene from acetone contains hemellitene (this vol., i, 418).

(II) *sym*-Trinitrobenzoic acid, which is not etherified by the action of alcoholic hydrogen chloride, even after treatment for 30 days, is readily converted into the methylic salt when its silver salt is heated with methylic iodide. Cetylic iodide also acts quite readily on the silver salt, producing the *cetylic salt*, which forms white crystals melting at 121—122°. It can be distilled in small quantities without undergoing decomposition. 1 : 2-Hydroxynaphthoic acid behaves in a similar manner. It appears, therefore, that the molecular volume of the alkyl radicle to be introduced by the action of the iodide on the silver salt does not affect the reaction.

(III) The best method to employ in order to ascertain whether an acid can be etherified or not by means of alcoholic hydrogen chloride is that originally proposed by E. Fischer, which consists in boiling the acid for three to five hours with alcohol containing 3 per cent. of hydrogen chloride.

(IV) Hemimellitic acid, $C_6H_3(COOH)_3$ [1 : 2 : 3], only yields a dimethylic ether in the cold, when it is treated with hydrogen chloride dissolved in methylic alcohol. When the reaction is carried out at a higher temperature, a small amount of the trimethylic salt is formed, its production being probably due to the preliminary formation of a certain amount of anhydride at the temperature of the experiment. A. H.

**Azimido Compounds. IV. Azimidouramidobenzoic acids and Azimidobenzoic acids.** By THEODOR ZINCKE and BRUNO HELMERT (*Annalen*, 1896, **291**, 313—342; compare this vol., i, 300).

—The object of the investigation has been already explained (*loc. cit.*); and the result at which the authors have arrived is to the effect that the azimidouramidobenzoic acids obtained by the action of nitrous acid on the amidouramidobenzoic acids,

$$[NH_2 : NH\cdot NHCONH_2 : COOH = 1 : 2 : 4 \text{ and } 1 : 2 : 5],$$

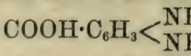
are most probably not identical; it is more likely that they are two different acids which give rise to the same azimidobenzoic acid.

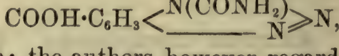
Metauramidobenzoic acid (Menschutkin, *Annalen*, 1870, **153**, 84), $COOH\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2$, crystallises from hot alcohol in aggregates of leaflets, and melts and decomposes at 269—270°; the *methylic* salt crystallises from glacial acetic acid in needles, and melts at 185°.

*Metauramidodibenzoic acid*, $CO(NH\cdot C_6H_4\cdot COOH)_2$, Griess' carbodibenzamic acid, is obtained by boiling an aqueous solution of barium *m*-uramidobenzoate; it is insoluble in common agents, and does not melt below 270°. Contrary to the statement of Sarauw (Abstr., 1882, 608) the ammonium salt is capable of existence in aqueous solution if excess of ammonia is present; the *methylic* salt crystallises from methylic alcohol in lustrous leaflets, and melts and decomposes at 223°.

4 : 3-*Nitrouramidobenzoic acid* is prepared by nitrating uramidobenzoic acid, and treating the mixture of dinitro-acids thus obtained with boiling ammonia; it is almost insoluble in ether and acetone, and crystallises from water in slender, yellow needles, which become red and decompose at 220°. The *ammonium* salt crystallises in lustrous, golden-yellow needles, and the *barium* salt, which dissolves sparingly in water, separates in small, yellow needles; the *methylic* salt crystallises from methylic alcohol in sulphur-yellow needles, and melts at 184°. The action of boiling water or boiling dilute acetic acid, during a protracted period, converts the acid into 4 : 3-nitramidobenzoic acid.

4 : 3-*Amidouramidobenzoic acid* is obtained by reducing nitrouramidobenzoic acid with tin and hydrochloric acid; it crystallises from water in small, slender needles, and does not melt below 270°. The *barium* salt dissolves somewhat readily in water, and crystallises in white needles; the silver salt rapidly darkens in light, and deposits silver when the solution in glacial acetic acid is boiled.

3 : 4-*Amidocarboxamidobenzoic acid*,  $COOH\cdot C_6H_3<{NH \atop NH}>CO$, is produced when the foregoing acid is treated with boiling water or boiling dilute hydrochloric acid (compare Griess, this Journal, 1872, 497); it is insoluble in common agents, and does not melt below 270°. The *ammonium* salt crystallises in white needles, and decomposes in absence of excess of ammonia; the barium and silver salts are amorphous, and the *methylic* salt separates from glacial acetic acid in the form of a fine powder.

Azimidometauramidobenzoic acid,  $COOH\cdot C_6H_3<{N(CONH_2) \atop \overline{\qquad\quad} N}\geqslant N$, has not been obtained in the pure state; the authors, however, regard it as distinct from the para-compound, and consequently represent its constitution by the foregoing expression. It is obtained by dissolving 4 : 3-amidouramidobenzoic acid in the minimum quantity of hot water, adding sodium nitrite to the cold solution, and then acidifying with hydrochloric acid; it is a white, amorphous powder, dissolving with great difficulty in ordinary organic solvents, excepting glacial acetic acid, and may be heated to 270° without undergoing fusion. On dissolving the acid in alkalis, it undergoes hydrolysis, yielding azimidobenzoic acid, carbonic anhydride, and ammonia; the same change is effected by boiling solvents.

Parauramidobenzoic acid is obtained from paramidobenzoic acid and potassium cyanate by the method adopted in preparing the meta-acid; although Griess (this Journal, 1872, 711) did not succeed in obtaining it crystalline, the acid separates as a white, crystalline powder, and does not melt below 270°. The *ammonium* salt crystallises in monoclinic plates, the *barium* and *silver* salts are amorphous, and the *methylic* salt crystallises from alcohol, and melts at 252°.

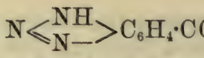
*Parauramidodibenzoic acid* arises from the foregoing acid when a solution of the barium salt is boiled during a protracted period; it is an amorphous substance, dissolving with great difficulty in common agents, and does not melt below 270°. The *ammonium* salt crystallises in lustrous leaflets, the *calcium*, *barium*, and *silver* salts are amorphous, and the *methylic* salt crystallises from methylic alcohol in small, white plates, which melt, evolving gas, at 246°.

*Dinitroparauramidobenzoic acid* is obtained by the action of fuming nitric acid on *p*-uramidobenzoic acid; it dissolves with difficulty in organic agents, becomes dark yellow at 190°, and melts at 268—270°. When treated with hot alkali, it yields 3 : 4-nitramidobenzoic acid. The *ammonium* salt is readily soluble in water.

3 : 4-*Nitrouramidobenzoic acid* is produced when the foregoing acid is treated with boiling ammonia, nitrous oxide being liberated; it crystallises from 50 per cent. acetic acid in small, yellow needles, and melts and decomposes at 221°. The *ammonium* salt dissolves readily in water, and the *barium* salt, which contains $3H_2O$, crystallises from water in slender, yellow needles; the *methylic* salt crystallises from methylic alcohol in small, yellow needles, and melts at 189°.

3 : 4-*Amidouramidobenzoic acid* crystallises from hot water in small, white needles, and does not melt below 270°; it is sparingly soluble in organic agents, and quickly reduces platinum tetrachloride. When the aqueous solution is boiled, 3 : 4-amidocarboxamidobenzoic acid (see above) is produced, the change being accelerated by the influence of hydrochloric acid. The *ammonium* salt crystallises in slender, white needles, and the *barium* salt, which dissolves readily in alcohol, also forms white needles; the *silver* salt is amorphous, and darkens rapidly when heated.

*Azimidoparauramidobenzoic acid*, $COOH\cdot C_6H_3{<}\begin{matrix}\overline{\qquad\quad N}\\ N(CONH_2)\end{matrix}{>}N$, is produced when 3 : 4-amidouramidobenzoic acid is treated with nitrous acid; it crystallises from a large volume of absolute alcohol in small needles, and does not melt below 270°. Treatment with boiling water, alcohol, or glacial acetic acid converts it into azimidobenzoic acid, and the same effect is produced by dissolution in cold alkalis.

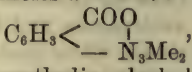
3:4-*Azimidobenzoic acid*,  $N{<}\begin{matrix}NH\\N-\end{matrix}{>}C_6H_4\cdot COOH$ [COOH : N : NH = 1 : 4 : 3 or 1 : 3 : 4], is produced by the action of sodium nitrite on an aqueous solution of orthodiamidobenzoic acid hydrochloride, and crystallises from water in small needles, and from glacial acetic acid in lustrous leaflets, which do not melt below 270°. The *sodium* salt separates from methylic alcohol in crystals containing the solvent, and the *barium* salt contains $4H_2O$; the *silver* salt dissolves in ammonia, and the *methylic* salt crystallises from methylic alcohol in rhombic plates, and melts at 170—171°. Azimidobenzoic acid also yields a *hydrochloride*, which dissolves very readily in water, and loses hydrogen chloride over sulphuric acid.

The *chloride* of *dimethylazammoniumbenzoic acid*,

$$COOH\cdot C_6H_3\cdot N_3Me_2Cl,$$

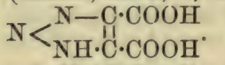
crystallises in slender, white needles, and melts and decomposes at 238°; the *platinochloride* crystallises in orange-yellow cubes and leaflets.

*Methylazimidobenzoic acid*, $COOH\cdot C_6H_3\cdot N_3Me$, is obtained by eliminating methylic chloride from the foregoing chloride; it crystallises from water in aggregates of very small needles, and melts above 270°.

The *betaïne* of *dimethylazammoniumbenzoic acid*,  $C_6H_3{<}\begin{matrix}COO\\ |\\ -N_3Me_2\end{matrix}$, is obtained by heating azimidobenzoic acid with methylic alcohol and the iodide, treating the liquid with water, and agitating with freshly prepared silver oxide; it crystallises from absolute alcohol in slender needles, and melts at 247°.

*Acetazimidobenzoic acid*, $COOH\cdot C_6H_3\cdot N_3Ac$, crystallises from alcohol in small needles, and melts and decomposes at 232°.

Both meta- and para-azimidouramidobenzoic acids yield azimidobenzoic acid when dissolved in ammonia, and the solution acidified after remaining for some time; carbonic anhydride is eliminated, and the acid thus obtained is identical in every respect with the substance obtained from 3 : 4-diamidobenzoic acid.

By oxidising azimidotoluene with potassium permanganate, Bladin (Abstr., 1893, i, 375) obtained 1 : 2 : 3-triazoledicarboxylic acid,  $N{<}\begin{matrix}N-C\cdot COOH\\ \|\\ NH\cdot C\cdot COOH\end{matrix}$. The same substance, which the authors call *azimidoethylenedicarboxylic acid*, or *osotriazonedicarboxylic acid*, is produced by dissolving azimidobenzoic acid in caustic soda, and oxidising it with a 10 per cent. solution of potassium permanganate.

M. O. F.

**Hydrated Sodium Salicylate.** By GYSBERT ROMYN (*Ned. Tydschr. Pharm, &c.*, 1896, 111—113).—Sodium salicylate, when dissolved in its own weight of water, after a time deposits large prismatic crystals showing double refraction, and containing $6H_2O$. If crystallisation will not readily set in, it may be promoted by introducing a crystal from a previous experiment.

As might be expected, the crystals very rapidly effloresce, and the water is quickly expelled on drying at 80°. L. DE K.

**Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Hydrocarbons of the Benzene Series in presence of Aluminium Chloride.** By LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 1062—1064.).—The action of ethylic chloroglyoxylate on benzene hydrocarbons in presence of aluminium chloride and carbon bisulphide yields a considerable quantity of the substituted glyoxylic salts, R·CO·COOEt. These are colourless liquids, with a disagreeable odour, and are very stable. Alcoholic potash converts them into resinous products, but aqueous soda gives an excellent yield of the corresponding sodium salts, from which the acids are readily obtained. The acids are crystallisable compounds only slightly soluble in water; they distil without change in a vacuum, but decompose when distilled in presence of air, as Claisen has shown, the products being carbonic oxide and anhydride and a mixture of aldehyde and acid.

The reaction of ethylic chloroglyoxalate on the benzene hydrocarbons is as general as that of the other acid chlorides, and can be extended to the mixed ethers of the aliphatic and benzene series, but not to the phenols nor their acid ethereal salts. As a general rule, when isomerides can be formed, the para-derivative is the chief product, if its formation is possible. C. H. B.

**Reduction of the Benzylaminecarboxylic [exo-Amidotoluic] acids.** By ALFRED EINHORN (*Ber.*, 1896, **29**, 1590—1594).—The substituted *exo*-amidotoluic acids are converted by reduction with amylic alcohol and sodium into two isomeric hexahydro-compounds, which are probably the *cis*- and *trans*-forms of the acid. The *cis*-compounds have probably a betaïne-like structure, and are not extracted from solution in amylic alcohol by dilute alkalis, so that the two can be separated in this manner.

The *cis*-acids are all basic oils with a stupefying odour, whilst the *trans*-acids are crystalline.

cis-exo-*Amidohexahydroparatoluic acid* forms a *hydrochloride* which crystallises in long, thin needles melting at 235°. The *platinochloride* melts at 208—209°, and the *aurochloride* at 215—217°.

exo-*Diethylamido-orthotoluic acid*, $NEt_2·CH_2·C_6H_4·COOH$, is prepared from diethylamine and orthochloromethylbenzamide. It melts at 105°, and yields a *platinochloride* melting at 200°, an *aurochloride* melting at 202°, and a *picrate* melting at 128°.

cis-exo-*Diethylamidohexahydro-orthotoluic acid* is an oil; the *hydrochloride* melts at 236—238°, the *aurochloride* at 190°, and the *platinochloride* at 198°. trans-exo-*Diethylamidohexahydro-orthotoluic acid* crystallises in long, slender needles melting at 97°, and is odourless. The *aurochloride* melts at 115°, and the *picrate* at 135°. These acids are accompanied by exo-*hydroxyorthotoluic acid*, $COOH·C_6H_{10}·CH_2·OH$, which melts at 113·5°.

exo-*Diethylamidoparatoluic acid* may be prepared from *exo*-chloroparatoluic acid and diethylamine. It forms crystals resembling those of salammoniac, and melts at 150°. The *hydrochloride* crystallises with $2H_2O$ in prisms and melts at 185°. The *aurochloride* melts at 156°, the *platinochloride* at 202—208°, and the *picrate* at 174—176°.

exo-cis-*Diethylamidohexahydroparatoluic acid* boils at 275—280°; the *hydrochloride* melts at 166—167°. The *hydrochloride* of the trans-*acid* melts at 195°, the *aurochloride* at 162—163°, and the *picrate* at 163—164°.

The *hydrochloride* of *hexahydrophenylamidoacetic acid* crystallises with 2 mols. of alcohol in needles, and melts at 232°. A. H.

**Isomerism of Ethylic Formylphenylacetate.** By WILHELM WISLICENUS (*Annalen*, 1896, **291**, 147—216; compare Abstr., 1895, i, 366; this vol., i, 369; and Claisen, this vol., i, 557).—The author emphasises his opinion that the two forms of ethylic formylphenylacetate are structurally isomeric in the sense already indicated (*loc. cit.*); throughout the description of his investigation, the α-salt refers to the liquid isomeride, which develops coloration with ferric chloride, and is regarded as having the constitution $OH{\cdot}CH{:}CPh{\cdot}COOEt$, whilst the solid isomeride, which is indifferent towards ferric chloride, and has the constitution $CHO{\cdot}CHPh{\cdot}COOEt$, is distinguished as the β-salt. A mixture of both isomerides is obtained by the action of sodium wire on ethylic phenylacetate and ethylic formate in dry ether; on extracting the liquid with water, and rendering acid the extract with sulphuric acid, a partially crystalline mass is obtained, from which the liquid isomeride may be removed by suction. Another method of purifying the crude product consists in adding aqueous copper acetate to the alcoholic solution, and decomposing with acid the copper derivative so obtained.

The α-salt, *ethylic hydroxymethylenephenylacetate* (*ethylic phenylhydroxyacrylate*), $OH{\cdot}CH{:}CPh{\cdot}COOEt$, boils at 135° and 145° under pressures of 15 mm. and 25 mm. respectively; a specimen containing no crystals of the solid modification, or one which has been heated at 70—80° during one hour, may be preserved indefinitely without undergoing molecular rearrangement, whilst the presence of the solid form induces conversion into this isomeride. The sp. gr. = 1·12435 at 15°/15°, and 1·12045 at 20°/20°.

The β-salt, *ethylic formylphenylacetate*, $CHO{\cdot}CHPh{\cdot}COOEt$, is purified by treating the crystals first obtained with chloroform or benzene, and finally with ether, until indifference towards ferric chloride indicates the complete removal of the α-modification. The melting point is approximately 70°, but is somewhat indefinite, owing to the production of a certain amount of the isomeride when the solid is heated. The pure salt may be preserved unchanged in closed tubes, and does not, as previously stated, undergo transformation into the isomeride unless subjected to the influence of moisture or the vapour of solvents. Determinations of the molecular weight, as in the case of the liquid form, are in agreement with the formula $C_{11}H_{12}O_2$; the sp. gr. = 1·271. The heat of combustion of the α-salt at constant volume is 1318·7 Cals. per gram-molecule, and 1319·8 Cals. under constant pressure; the corresponding values for the β-modification are 1315·5 Cals. and 1316·4 Cals. respectively.

The striking difference in behaviour towards ferric chloride exhibited by the two forms, has enabled the author to investigate systematically the influence of solvents on the transformation of one into the other. When either modification is dissolved in alcohol, the solution very soon contains both forms, until, after two days, a condition of equilibrium is reached, and the liquid, whether obtained originally from the α- or the β-salt, exhibits the same intensity of coloration with ferric chloride. Other solvents, however, do not yield a solution containing equal quantities of the two salts, the proportion of each existing in the liquid when the condition of equilibrium is attained, depending entirely on the nature of the medium, and the temperature and concentration of the solution; thus methylic alcohol, a solvent of high dissociating power, is favourable to the existence of the β-salt, whilst solutions in chloroform and benzene contain only the α-modification, the influence of high temperature and an increased degree of concentration being in the same direction. The results of a spectrochemical investigation, carried out by Brühl, establish the formula already ascribed to the α-salt, and indicate that an alcoholic solution of the β-salt contains, in reality, both modifications; the specific magnetic rotatory power of the α-salt is 2·0369 at 15°, and of the β-salt, dissolved in benzylic alcohol, 2·1047 at 17·5°; the experiments carried out by Perkin leading to the same conclusion as those on the molecular refraction. Traube's determinations of the molecular solution volumes establish the constitution of the α-salt, and yield results which are not in agreement with the aldehydic formula for the β-modification; an explanation of the latter fact is probably to be found in the existence of one-third or a half of the β-salt in the form of complex molecules when dissolved.

The *acetate* of ethylic hydroxymethylenephenylacetate,

$$\mathrm{OAc{\cdot}CH{:}CPh{\cdot}COOEt},$$

is produced when either salt is heated with acetic anhydride for one hour at 160°; it is a transparent oil, which boils at 184° under a pressure of 18 mm. The *dibromide*, $\mathrm{OAc{\cdot}CHBr{\cdot}CPhBr{\cdot}COOEt}$, crystallises from dilute alcohol in small, lustrous prisms, and melts at 67°. The *benzoate* of ethylic hydroxymethylenephenylacetate, $\mathrm{OBz{\cdot}CH{:}CPh{\cdot}COOEt}$, is obtained from both salts, and crystallises from alcohol in large, lustrous, rhombohedra melting at 87—88°; the production of one acetate and benzoate from the two modifications is an argument in favour of a structural difference between the original salts.

Phenylic cyanate is advantageously applied in distinguishing between hydroxy-derivatives and ketones or aldehydes, being indifferent towards the latter groups, and uniting with the former to produce ethereal carbanilides. In the present instance, it is found that the β-salt is indifferent towards the agent, whilst on remaining with it in a sealed tube during several months, the α-modification yields the *carbanilido*-derivative of ethylic hydroxymethylenephenylacetate, $\mathrm{NHPh{\cdot}CO{\cdot}O{\cdot}CH{:}CPh{\cdot}COOEt}$; it crystallises from alcohol in microscopic leaflets, and melts at 116°. In an analogous manner, Claisen's hydroxymethylenebenzylic cyanide, obtained by the action of sodium on benzylic cyanide and ethylic formate, yields the *carbanilido*-derivative, $\mathrm{NHPh{\cdot}CO{\cdot}O{\cdot}CH{:}CPh{\cdot}CN}$, which crystallises from alcohol in small needles, and melts at 153—154°; it develops no coloration with ferric chloride, but when heated above the melting point, phenylic cyanate is eliminated, and the product develops colour with ferric chloride.

A remarkable feature of the isomerism of ethylic formylphenylacetate is to be found in the fact that this isomerism is probably extended to the metallic derivatives; thus two distinct copper derivatives have been isolated, and there are satisfactory indications that the α-sodium salt undergoes conversion into an isomeride which exists only in solution. Although the author does not claim to have established this principle, he regards the evidence brought forward as opposed to Nef's hypothesis (this vol., i, 71) that metallic derivatives of acidic substances do not exist, having the metal directly united with carbon.

The *α-sodium* derivative of ethylic hydroxymethylenephenylacetate is obtained as a white powder, which melts indefinitely at 120°, on adding sodium wire to an ethereal solution of the liquid ethylic salt; on treating the dry substance with dilute sulphuric acid, the α-ethylic salt is liberated; but, if excess of the acid is added to an aqueous solution which has remained at the ordinary temperature during one minute, the β-ethylic salt separates immediately in crystals. When carbonic anhydride is led into the solution of either ethylic salt in aqueous soda, the α-ethylic salt separates first, a few crystals of the solid modification being formed when the operation has proceeded during a protracted period; dilute sulphuric acid in small portions, and added slowly, effects the same result; but if the agent is added in excess, the precipitate consists exclusively of the solid form. On treating the solid sodium derivative with ferric chloride, a deep bluish-violet mass is produced, which probably consists of the α-ferric derivative, the solution in alcohol being bluish-violet; the aqueous solution of the sodium derivative, however, although rendered bluish-violet by ferric chloride, becomes much less intensely coloured, and no separation of ferric derivative occurs, whilst after a few minutes, the colour disappears, and the β-ethylic salt separates.

The *α-copper* derivative of ethylic hydroxymethylenephenylacetate, $C_{22}H_{22}O_6Cu$, obtained on adding aqueous copper acetate to an alcoholic solution of the α-ethylic salt, crystallises from hot alcohol in lustrous, green needles containing 2 mols. of ethylic alcohol; it rapidly effloresces in air and at 80°, melting at 171—173°. On dissolving the substance in hot alcohol, a small quantity of an insoluble, dark green *compound* is produced having the composition $C_{13}H_{16}O_4Cu$. The *β-copper* derivative is obtained on treating an aqueous solution of the sodium derivative with copper sulphate, the solutions being previously cooled with ice; a bright bluish-green precipitate is formed which yields the β-ethylic salt exclusively when decomposed with sulphuric acid. At ordinary temperatures, and in the dry state, this modification becomes spontaneously converted into the α-isomeride, and, although insoluble in alcohol, the hot agent rapidly produces a green solution, from which the α-derivative crystallises on cooling. M. O. F.

**Spectrochemical Investigation of α- and β-Ethylic Formylphenylacetates.** By JULIUS W. BRÜHL (*Annalen*, 1896, **291**, 217—

225).—The author has determined the molecular refraction and dispersion of the two forms of ethylic formylphenylacetate, described by W. Wislicenus (preceding abstract). His investigation shows that both forms exist in solution, and whilst the liquid $\alpha$-salt is accurately represented by the formula $OH{\cdot}CH{:}CPh{\cdot}COOEt$, the constitution of the solid isomeride may be expressed with equal truth by the formula $CHO{\cdot}CHPh{\cdot}COOEt$, or by the geometrically isomeric form of the structure ascribed to the $\alpha$-salt. M. O. F.

**Halogen Derivatives of the Sulphonamides.** By J. H. KASTLE, B. C. KEISER, and ERNEST BRADLEY (*Amer. Chem. J.*, 1896, **18**, 491—502).—The compounds here described behave like substitution, rather than additive, derivatives of the sulphonamides; for instance, they explode when rapidly heated, the halogen being evolved, and they are decomposed by strong acids with liberation of the halogen and formation of the sulphonamide; in these two respects, they recall the behaviour of nitrogen trichloride. Furthermore, they are oxidising agents by virtue of the fact that they readily part with their halogen, the original sulphonamide being formed; if they were additive compounds, their oxidising power would be equivalent to that of 1 atom of oxygen, whereas it is found to be equivalent to that of 2 atoms, showing that the compounds are substitution compounds. These collateral evidences are necessary, since analysis cannot be depended on to detect the 2 atoms of hydrogen which constitute the difference between the additive and substitution products.

*Benzenedichlorosulphonamide*, $C_6H_5{\cdot}SO_2{\cdot}NCl_2$, is prepared by passing a rapid current of chlorine through a solution of benzenesulphonamide in the smallest possible quantity of aqueous soda (1 : 10); the precipitate is purified by being heated with water, when the chlorine derivative melts, and may be thus separated from unchanged sulphonamide; dissolution in alcohol and precipitation by water complete the purification. It forms nacreous laminæ, melts at 70°, and explodes at 218—220°. *Paratoluenedichlorosulphonamide* was prepared in a similar manner; it melts at 80°, and explodes at high temperatures. *Parabromobenzenedichlorosulphonamide* is a white, crystalline powder, melting at 106°.

*Benzenedibromosulphonamide*, prepared by adding bromine to a solution of benzenesulphonamide in aqueous soda, forms dark yellow laminæ, melts at 110°, evolving some bromine, and explodes when heated suddenly; it is readily soluble in alcohol, ether, chloroform, and carbon bisulphide. *Parachlorobenzenedibromosulphonamide* is a yellow, crystalline substance. A. G. B.

**Oxidation of Hydroxylamine by Benzenesulphonic Chloride.** By OSCAR PILOTY (*Ber.*, 1896, **29**, 1559—1567).—The compounds $(Ph{\cdot}SO_2)_2N{\cdot}OH$, dibenzenesulphonehydroxylamide, and $(Ph{\cdot}SO_2)_3NO$, tribenzenesulphonehydroxylamide, are already known; the author has prepared the missing member of the series, $Ph{\cdot}SO_2{\cdot}NH{\cdot}OH$, *benzenesulphonylhydroxylamide* (*benzsulph-hydroxamic acid*), by adding benzenesulphonic chloride to an alcoholic solution of hydroxylamine; it melts at about 126°, and has but very feeble acid properties, not even liberating carbonic anhydride from hydrogen carbonates; its *potassium* and *sodium salts* were obtained by adding the alkali methoxides to an alcoholic solution of the acid. It yields a *diacetyl* derivative melting at 85°. Ferric chloride, and also bleaching powder or iodine, oxidise it quantitatively to dibenzenesulphonhydroxylamide acid and nitrous acid; fuming nitric acid oxidises it, although not quantitatively, to tribenzenesulphonhydroxylamide. When it is shaken with 40 per cent. aqueous potassium hydroxide, potassium benzenesulphonate separates, and, by acidifying the solution with acetic acid and adding silver nitrate, a precipitate of silver hyponitrite, mixed with acetate, is obtained; in fact, this is probably the best way of preparing silver hyponitrite. It is thus seen that the action of benzenesulphonic chloride on hydroxylamine may be regarded as an oxidation of the latter taking place in two stages; the hydroxylamine is eventually oxidised to hyponitrous acid, whilst the sulphonic chloride is reduced to a sulphinic acid.

Phenylhydroxylamine brings about a similar series of reactions, yielding *benzenesulphonphenylhydroxylamide*, $Ph{\cdot}SO_2{\cdot}NPh{\cdot}OH$, melting at 121°, and then benzenesulphinic acid and nitrosobenzene, $Ph{\cdot}NO$. Benzylhydroxylamine, however, only yields the intermediate product *benzenesulphonobenzylhydroxylamine*, $Ph{\cdot}SO_2{\cdot}N(CH_2Ph){\cdot}OH$, melting at 92—93°; the action of sodium hydroxide on this yields only benzaldoxime.

The author has also obtained hyponitrous acid in the solid state, and its ammonium salt too (compare Hantzsch, this vol., ii, 520).

C. F. B.

**Orthamidobenzophenone.** By Carl Graebe and F. Ullmann (*Annalen*, 1896, **291**, 8—16; compare Abstr., 1895, i, 147).—The paper is an expansion of the preliminary note on the preparation of orthamidobenzophenone and synthesis of acridone (*loc. cit.*).

M. O. F.

**Condensation of Benzaldehyde with Acetophenone.** By Stanislaus von Kostanecki and G. Rossbach (*Ber.*, 1896, **29**, 1488—1494).—When benzaldehyde is condensed with acetophenone in presence of sodium hydroxide, the resulting product depends largely on the conditions of the experiment.

*Benzylideneacetophenone*, $CHPh{:}CH{\cdot}COPh$, is produced when 20 grams of a 10 per cent. solution of sodium hydroxide is added to an alcoholic solution of 21 grams of benzaldehyde and 24 grams of acetophenone, and the reaction allowed to proceed during 24 hours.

*Benzylidenediacetophenone*, $CHPh(CH_2{\cdot}COPh)_2$, is formed when the reacting substances are in the proportion of 1 mol. of benzaldehyde and 2 mols. of acetophenone. It forms thick prisms, melting at 85°. By distillation, it is decomposed into benzylideneacetophenone and acetophenone.

When 2 mols. of benzaldehyde react with 3 mols. of acetophenone for 24 hours at 40—50°, a substance of the formula $C_{38}H_{32}O_3$, melting at 198°, is produced; if, however, the temperature is raised to 100°, an isomeric substance, melting at 256°, is formed. These are evidently the two stereoisomeric dibenzylidenetriacetophenones,

$$COPh{\cdot}CH(CHPh{\cdot}CH_2{\cdot}COPh)_2.$$

*Dibenzylidenetriacetophenone* is a crystalline powder melting at 198°, and very insoluble in alcohol, although easily soluble in acetic acid and warm benzene. When suspended in alcohol and heated on the water bath, after addition of concentrated sodium hydroxide, it is converted into its isomeride, melting at 256°.

*Dibenzylidenetriacetophenone* crystallises in glistening plates and melts at 256°; by distillation, it is decomposed into benzylideneacetophenone and acetophenone. J. F. T.

**Action of Alkali on Benzylideneacetophenone and Benzylidenediacetophenone.** By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1896, **29**, 1495—1497; compare preceding abstract).—The two isomeric dibenzylidenetriacetophenones are formed by the condensation of benzylideneacetophenone and acetophenone in the presence of sodium hydroxide, the higher (256°) melting compound being formed at a temperature not higher than 40—50°, the lower (198°) at the temperature of the boiling water bath. They are also produced by the action of sodium hydroxide on benzylideneacetophenone without the addition of acetophenone.

In order to show that the dibenzylidenetriacetophenones were additive products of benzylideneacetophenone and benzylidenediacetophenone, and were not formed by the simple rearrangement of the atoms in benzylideneacetophenone, they were made by condensing benzylidenediacetophenone with benzylideneacetophenone in the presence of sodium hydroxide, a very fair yield being obtained. It is, therefore, evident that unsaturated, as well as 1 : 5-diketones, which contain a methylene group next to the carbonyl, are transformed by the action of alkalis into the more stable 1 : 7-triketones.

A good test for the purity of 1 : 5-diketones is the action of concentrated sulphuric acid on them; whereas unsaturated ketones give in this way an orange-yellow colour, the 1 : 5-diketones remain colourless or become slightly yellow (with blue fluorescence), whilst the 1 : 4 : 7-triketones become red. J. F. T.

**1 : 3-Diketones.** By LUDWIG CLAISEN (*Annalen*, 1896, **291**, 25—137; compare Abstr., 1894, i, 31). I. [With L. FALK.]—The paper deals with monobenzoyl derivatives of 1 : 3-diketones, substances which present two possibilities in considering the question of structure. In most cases both isomerides, corresponding with the groups $-C(OH){:}\underset{|}{C}\cdot CO-$ and $-CO\cdot\underset{|}{C}H\cdot CO-$, have been isolated, and are distinguished as the $\alpha$-, or acidic, and the $\beta$-, or neutral modification respectively.

The existence of this isomerism has been contested by Nef, who regards the variation in properties of the two forms as depending on differences of a physical character; in opposition to this view, however, the authors adduce the following facts. (1) Cryoscopic determinations in benzene of the molecular weight of both modifications of dibenzoylacetylmethane yield identical results, and stability of the two forms in this solvent has been already established. (2) The differences in chemical properties exhibited by the isomerides, as, for instance, their behaviour towards ferric chloride and alkali carbonates, characterise, not only the solid substances, but also their solutions.

The authors expound their views on the subject of this isomerism, which they regard as structural in character.

The preparation of dibenzoylmethane has been hitherto attended with some difficulty, and a method is described by which the yield may be raised to 80 or 90 per cent. of the theoretical quantity. Improvements have been also effected in the production of benzoylacetylmethane from benzoylacetone, the modification consisting in the employment of an alcoholic solution of the sodium derivative of the diketone, instead of suspending the solid substance in ether; another convenient mode of benzoylating diketones is an application of the process described by Claisen (Abstr., 1895, i, 139), the substance being treated with 1 mol. of benzoic chloride in presence of 2 or 3 mols. of dry sodium carbonate. These methods have been applied successfully in preparing dibenzoylacetylmethane, benzoyldiacetylmethane, ethylic benzoylacetoacetate, and ethylic benzoylmalonate.

*α-Dibenzoylacetylmethane*, $CBz_2{:}CMe{\cdot}OH$ (compare Nef, Abstr., 1894, i, 31), is obtained, in the manner already indicated, from benzoylacetone, benzoic chloride, and sodium carbonate, the triketone being liberated by means of acetic acid; it separates from petroleum in short, colourless prisms, belonging to the monoclinic system; $a : b : c = 1{\cdot}0271 : 1 : 4{\cdot}8560$, and $\beta = 121° 54'$. It melts almost completely at 80—85°, solidifies at 87—89°, and melts again at 99—101°; these phenomena are exhibited less definitely by an uncrystallised specimen, and as they probably depend on an isomeric change, the authors regarded it as probable that the freshly precipitated substance contains a certain amount of a hydrate yielding the isomeride below the melting point of the α-modification, but this view was negatived by experiment.

*β-Dibenzoylacetylmethane*, $CHAcBz_2$, is obtained by boiling a solution of the α-modification in 50 per cent. alcohol, and allowing the liquid to cool spontaneously; it crystallises in snow-white needles, and melts at 107—110°, no indication of initial fusion at 80—85° being observed. The conversion of one modification into the other is not completely effected by absolute alcohol, the α-triketone crystallising for the most part unchanged; the greater the dilution of the solvent, however, the more complete is the transformation. Careful cryoscopic determinations have established the identity of the molecular weight of the two forms; the experiments were conducted in benzene, it having been previously shown that no molecular rearrangement occurs in this medium. Whilst α-dibenzoylacetylmethane develops a red coloration with ferric chloride, and exhibits marked acidic properties, the β-modification is indifferent to the agent, and has no power to form salts; on remaining in contact with alkalis, however, it dissolves slowly, but the salts produced in this manner yield the α-triketone on acidification. The copper derivative is also that of the latter modification, although Wislicenus (compare this vol., i, 554) has obtained different copper derivatives from the two modifications of ethylic formylphenylacetate.

The two forms of dibenzoylacetylmethane are anhydrous, and whilst the β-isomeride may be preserved for any period without undergoing change, the α-triketone slowly passes into the neutral form, the transformation being almost complete at the end of three or four months; after the lapse of a year, 100 grams of the α-modification was found on examination to consist of a mixture of 80 grams of the β-triketone, 8 grams of the original form, and 12 grams of dibenzoylmethane. At 85°, the acidic form is converted almost quantitatively into the isomeride, whilst at 110° the reverse transformation takes place to the extent of 75 per cent. of the material employed. When heated at 260—280°, both modifications yield dibenzoylmethane and acetic acid. Although β-dibenzoylacetylmethane is prepared by boiling a solution of the isomeride in dilute alcohol, and allowing the liquid to cool spontaneously, this result is not effected when the solution is cooled suddenly, 90 per cent. of the α-triketone under these conditions separating unchanged; either modification, when dissolved in hot absolute alcohol, yields a crystalline mixture of the isomerides, of which the α-form constitutes two-thirds, and the β-triketone one-third. Whilst the action of acetone is exactly similar to that of alcohol (80 per cent. of the α-form being obtained) acetic acid exerts a hydrolytic action, converting the α-triketone into dibenzoylmethane and acetic acid.

*Benzoylparabromobenzoylacetylmethane* is obtained in the acidic form from benzoylacetone, parabromobenzoic chloride, and potassium carbonate; it crystallises from alcohol in short prisms, and melts at 105—106°. Ferric chloride develops an intense red coloration, and copper acetate precipitates the blue *copper* derivative. The neutral modification does not exist.

Tribenzoylmethane (compare Claisen, Abstr., 1894, i, 192) occurs in two modifications, the α-form, which melts at 210—220°, passing into the β-isomeride, which crystallises in slender needles, and melts at 223—226° after sintering at 215°. The spontaneous transformation of α-tribenzoylmethane into the β-form is more rapid than in the case of dibenzoylacetylmethane; 30 per cent. is converted during 20 hours, and the rearrangement is complete at the end of 60 hours, or at 100° after one hour. Treatment with alcohol or acetone converts the α-compound immediately into the β-form, and the transformation is almost as rapid when the substance is covered with methylic alcohol, ether, or glacial acetic acid; the acidic form is more stable, however, in chloroform or benzene, and separates unchanged after dissolution during eight hours.

*α-Parabromobenzoyldibenzoylmethane* melts at 186—189°, and, when the alcoholic solution is boiled, yields the β-modification which melts at 206—208°, the conversion of one form into the other being less rapid than in the case of tribenzoylmethane.

Dibenzoylated acetylacetone (Abstr., 1894, i, 31 and 32), the benzoate of benzoyldiacetylmethane, may also be prepared by the alkali carbonate method. When heated with aniline on the water bath it yields the *anilide*, $CAcBz{:}CMe{\cdot}NHPh$, which crystallises from methylic alcohol in short, canary-yellow prisms, and melts at 87—89°; it dissolves in alkalis, and is reprecipitated by carbonic anhydride.

Dibenzoylated benzoylacetone, the benzoate of acetyldibenzoylmethane, has been described as an oil; by the new method, however, it is obtained as a solid substance which crystallises from alcohol in flat, colourless prisms, and melts at 87—88°. The action of alkalis gives rise to dibenzoylacetylmethane and benzoic acid, whilst aniline converts it into the *anilide*, $\mathrm{CBz_2{:}CMe{\cdot}NHPh}$, which crystallises in slender, straw-yellow needles, and melts at 166—167°.

*Dibenzoylated dibenzoylmethane*, the *benzoate of tribenzoylmethane*, $\mathrm{CBz_2{:}CPh{\cdot}OBz}$, is prepared from the β-triketone and benzoic chloride (1 mol.) under the influence of sodium carbonate; it is obtained in lustrous, transparent crystals by adding petroleum to the solution in ethylic acetate, and melts at 121—122°. The substance is also produced by the action of benzoic chloride on the sodium derivative of tribenzoylmethane (compare W. H. Perkin, jun., Trans, 1885, **47**, 253), the product of high melting point, which Perkin regarded as tetrabenzoylmethane, not having been obtained in subsequent experiments. The *anilide* of tribenzoylmethane,

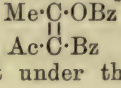
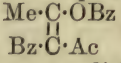
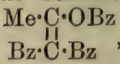
$$\mathrm{CBz_2{:}CPh{\cdot}NHPh},$$

is obtained by the action of aniline on the benzoate; it crystallises from alcohol in short, yellow prisms, and melts at 140—142°.

The *parabromobenzoate* of *tribenzoylmethane*,

$$\mathrm{CBz_2{:}CPh{\cdot}O{\cdot}CO{\cdot}C_6H_4Br},$$

crystallises in colourless prisms, and melts at 155—156°. The *α-naphthoate* separates from ethylic acetate, on adding petroleum, in short, lustrous prisms, and melts at 150—151°.

Although the treatment of benzoyldiacetylmethane, dissolved in ethylic acetate, with benzoic chloride in presence of potassium carbonate, gives rise to the benzoate which melts at 102—103° (Abstr., 1894, i, 32), an isomeric *compound* is produced when the action is carried out with benzoic chloride and pyridine; it crystallises from petroleum in flat, lustrous prisms, and melts at 66—67°, being considerably more soluble than the isomeride. It undergoes conversion into the triketone of higher melting point when heated on the water bath, and after remaining at 120° during 12 hours, 60 per cent. of the material was found to become transformed; both modifications have the molecular weight corresponding with the formula $\mathrm{C_{19}H_{16}O_4}$, and neither substance develops a red coloration with ferric chloride. The character of this isomerism is most probably stereochemical, the compounds in question being represented by the formulæ  $\begin{matrix}\mathrm{Me{\cdot}C{\cdot}OBz}\\ \|\\ \mathrm{Ac{\cdot}C{\cdot}Bz}\end{matrix}$ and  $\begin{matrix}\mathrm{Me{\cdot}C{\cdot}OBz}\\ \|\\ \mathrm{Bz{\cdot}C{\cdot}Ac}\end{matrix}$; this view is supported by the fact that under the same conditions of treatment with benzoic chloride, acetyldibenzoylmethane yields but one benzoate,  $\begin{matrix}\mathrm{Me{\cdot}C{\cdot}OBz}\\ \|\\ \mathrm{Bz{\cdot}C{\cdot}Bz}\end{matrix}$, melting at 87—88°, the structure of this substance obviously excluding the possibility of stereoisomerism. Development of this method of benzoylation has revealed the fact that in the case of diketones and ethereal salts of 1 : 3-diketonic acids, derivatives are invariably obtained in which the benzoic radicle is directly united with oxygen, whilst the action of benzoic chloride on the alkali derivatives gives rise to benzoates having the acidyl group combined with carbon.

II. [With J. Bishop Tingle and C. Kerstiens.]—As in the case of the triketones already described, the ethereal salts of mesityloxidoxalic acid, $CMe_2\!:\!CH\cdot CO\cdot CH_2\cdot CO\cdot COOH$, occur in acidic and neutral forms. The latter, distinguished as the $\beta$-modifications, are obtained by a general method in which a mixture of mesitylic oxide and the ethereal oxalate is added to ether covering sodium wire; treatment with alcoholic sodium ethoxide converts the neutral into the acidic, or $\alpha$-modifications.

*Ethylic $\beta$-mesityloxidoxalate*, $CMe_2\!:\!CH\cdot CO\cdot CH_2\cdot CO\cdot COOEt$, is obtained in the manner indicated from mesitylic oxide and ethylic oxalate. It crystallises from petroleum in thin, four-sided plates and short, flat prisms, and melts at 59—60°; under pressures of 11 mm. and 40 mm. it boils at 143° and 165° respectively, and under atmospheric pressure at 260—263°. Ferric chloride and ferrous sulphate do not develop coloration with the substance, and no precipitate is formed with zinc or copper acetates; the salt is insoluble in a dilute solution of sodium carbonate, and gaseous ammonia yields no precipitate when led into its ethereal solution. *Methylic $\beta$-mesityloxidoxalate* crystallises from petroleum in leaflets, and from ether in short prisms; it melts at 67°, and in its behaviour towards chemical agents resembles the ethylic salt.

*$\beta$-Mesityloxidoxalic acid* is obtained by hydrolysing the ethylic salt, and crystallises from water in tough, vitreous prisms; it melts and evolves gas at 166—167°, dissolves readily in alcohol and with difficulty in benzene, being moderately soluble in ether, chloroform, and ethylic acetate. Hot aqueous potash resolves it into oxalic acid and mesitylic oxide, the latter being converted into acetone when the treatment with alkali is prolonged.

*Ethylic $\alpha$-mesityloxidoxalate*, $CMe_2\!:\!CH\cdot CO\cdot CH\!:\!C(OH)\cdot COOEt$, is obtained by the action of alcoholic sodium ethoxide on the $\beta$-modification, a crystalline specimen being most readily produced by decomposing the copper derivative; it melts at 21—22°, and, when heated on the water bath, is gradually transformed into the $\beta$-salt. The *copper* derivative contains $1H_2O$, and crystallises from benzene in dark green, silky needles, which melt and decompose at 165°; the *ferrous* derivative crystallises in small, blue needles, and the *ferric* derivative separates in brownish-red crystals, and melts at 140—141°. The *ammonium* derivative is formed when gaseous ammonia is led into the ethereal solution; it is a crystalline powder, and melts at 95°. *Methylic $\alpha$-mesityloxidoxalate* is produced when the $\beta$-salt is treated with sodium methoxide dissolved in methylic alcohol; it crystallises in yellowish prisms, and melts at 83—84°. In behaviour, it closely resembles the ethylic salt, developing coloration with ferric chloride, ferrous sulphate, and copper acetate; the *ammonium* derivative melts at 78—80°.

*$\alpha$-Mesityloxidoxalic acid* is produced when the $\beta$-acid is heated during a short period on the water bath with aqueous soda (2 mols.) or with an alcoholic solution of sodium ethoxide; the most con-

venient method, however, is hydrolysis of the methylic salt. When crystallised from benzene, it contains $1H_2O$, and in this condition melts at 92—93°, evolving gas at 110°, above which temperature it solidifies, and melts finally at 160—166°, the melting point of the $\beta$-acid. When heated on the water bath during three or four minutes, it undergoes conversion into the isomeride, the same result being effected on attempting to crystallise the substance from boiling water; the anhydrous acid melts at 84—86°, solidifies at 110°, and finally fuses at 164—166°, showing that the crystalline hydrated form is not merely the hydrate of the $\beta$-acid. Towards ferric chloride, ferrous sulphate and copper acetate, the acid behaves in a manner resembling the ethereal salts. Aniline salts of the two forms are obtained when an alcoholic solution of the base is mixed with the acid, but, in the case of the $\alpha$-modification, the liquid becomes yellow when heated, and addition of petroleum induces the crystallisation of the *anilido-acid*, $CMe_2\colon CH\cdot CO\cdot CH\colon C(NHPh)\cdot COOH$ or

$$CMe_2\colon CH\cdot CO\cdot CH_2\cdot C(\colon NPh)\cdot COOH,$$

which separates in lustrous, yellow prisms and melts at 120—121°; it dissolves readily in alkali carbonates, and the solution in concentrated sulphuric acid is magenta-red.

*Oxalyldimesitylic oxide*,

$$CMe_2\colon CH\cdot CO\cdot CH_2\cdot CO\cdot CO\cdot CH_2\cdot CO\cdot CH\colon CMe_2, \text{ or}$$
$$CMe_2\colon CH\cdot CO\cdot CH\colon C(OH)\cdot CO\cdot CH_2\cdot CO\cdot CH\colon CMe_2, \text{ or}$$
$$CMe_2\colon CH\cdot CO\cdot CH\colon C(OH)\cdot C(OH)\colon CH\cdot CO\cdot CH\colon CMe_2,$$

is a product of the action of mesitylic oxide (2 mols.) on ethylic oxalate in presence of sodium; it crystallises from alcohol in canary-yellow needles, and melts at 149—150°. The substance dissolves readily in dilute alkalis (compare Brühl, this vol., i, 522).

M. O. F.

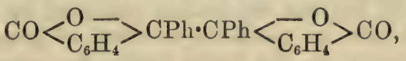
**Action of Thiophenol [Phenylic Hydrosulphide] on Aromatic Diketones.** By JULIUS TROEGER and A. EGGERT (*J. pr. Chem.*, 1896, [2], **53**, 478—483; compare Abstr., 1885, 748; 1887, 126).—When benzil is heated with twice its weight of thiophenol and zinc chloride for 10 hours on the water bath, deoxybenzoïn and phenylic bisulphide are produced. An *additive* compound of quinone and thiophenol, $C_6H_4O_2 + 2C_6H_5\cdot SH$, the analogue of Nietzki's phenoquinone, separates from mixed solutions of quinone and thiophenol in light petroleum; it forms orange-red crystals and is easily sublimed, the quinone being, however, partially separated during the process. Similar products were obtained by substituting parathiocresol and ethylic hydrosulphide for thiophenol. A. G. B.

**Orthodinitrodibenzylbenzidine and some Derivatives.** By FRANCIS E. FRANCIS (*Ber.*, 1896, **29**, 1450—1453).—*Orthodinitrodibenzylbenzidine*, $C_{12}H_8(NH\cdot CH_2\cdot C_6H_4\cdot NO_2)_2$, is prepared by heating benzidine with orthonitrobenzylic chloride in alcoholic solution; it is a red powder, and melts and decomposes at 226—227°; the *sulphate*, with $2H_2SO_4$, melts and decomposes at 215°. Tin and hydrochloric acid reduce it to benzidine and orthotoluidine, but a small quantity of the corresponding diamine, melting at 185°, is obtained when the reduction is effected with zinc dust and acetic acid at 20°. The dinitro-compound yields a yellow or red *dinitroso*-derivative, melting at 204°, and a grey *diformyl derivative*, melting at 205°. The latter is reduced by zinc dust and acetic acid at 20° to yellowish-white *diphenylenebisdihydroquinazoline*, $C_{12}H_8\left(<\begin{smallmatrix}-CH_2-\\CH\cdot NH\end{smallmatrix}>C_6H_4\right)_2$, melting above 200°; the *hydrochloride* (with 2HCl) and *platinochloride* were prepared. C. F. B.

**Reduction of Orthobenzoylbenzoic acid.** By F. Ullmann (*Annalen*, 1896, **296**, 17—25).—Rotering reduced orthobenzoylbenzoic acid during 13 days with sodium amalgam, and obtained orthobenzhydrylbenzoic lactone, which further reduction (8—10 days) converts into orthobenzylbenzoic acid, and the same result is brought about when zinc and hydrochloric acid are employed.

The author has attempted to obtain orthobenzylbenzoic acid by reducing orthobenzoylbenzoic acid with hydriodic acid and red phosphorus. On heating the substance in sealed tubes with these agents, however, it becomes completely charred at 160—180°, whilst at a lower temperature (140—150°), a small quantity of anthracene is produced; at this temperature, hydriodic acid, diluted with its own bulk of water, gives rise almost exclusively to anthracene.

The *dilactone* of *dihydroxytetraphenylethanedicarboxylic acid*,



$$CO<\begin{smallmatrix}O\;-\\C_6H_4\end{smallmatrix}>CPh\cdot CPh<\begin{smallmatrix}-\;O\\C_6H_4\end{smallmatrix}>CO,$$

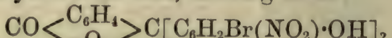
is obtained by heating orthobenzoylbenzoic acid with hydriodic acid and yellow phosphorus in a reflux apparatus for four or five hours at 127° in an atmosphere of carbonic anhydride; if the latter condition is not observed, the greater part of the acid remains unaltered, whilst a very small quantity of the lactone is produced, along with anthracene and anthraquinone. It is insoluble in most solvents, but dissolves readily in boiling toluene, aniline, and glacial acetic acid, from which it separates in small plates, melting at 265°. Alkalis convert the lactone into a mixture of orthobenzoylbenzoic and orthobenzhydrylbenzoic acids.

The latter substance is conveniently prepared from orthobenzoylbenzoic acid by reduction with zinc and dilute acetic acid, the lactone separating as the solution cools. Further reduction of the lactone with hydriodic acid and yellow phosphorus converts it into orthobenzylbenzoic acid. M. O. F.

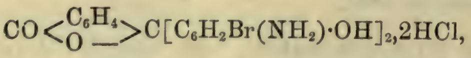
**Ethers of Phenolphthaleïn.** By Ernesto Grande (*Gazzetta*, 1896, **26**, i, 222—231).—On leaving a mixture of anisoïl, phthalic anhydride, and aluminium chloride for several days, driving off the hydrogen chloride at 100°, and pouring into water, a product is obtained, from which soda dissolves anisoïlphthaloylic acid (Nourisson, Abstr., 1886, 1029), leaving a residue of the dimethyl ether of phenolphthaleïn, $C_{22}H_{18}O_4$, which von Baeyer prepared by the action of methylic iodide on alkaline phenolphthaleïn (Abstr., 1880, 650), but did not describe further. It crystallises in colourless, lustrous laminæ, melting at 101—102°, and is soluble in acetic acid, chloroform, or carbon bisulphide, but insoluble in water; it is precipitated unaltered from its sulphuric acid solution by water, but not if the solution has been heated to 80—90°. It does not react with hydroxylamine, and consequently has the lactonic constitution. When heated with aqueous potash, it is converted into *potassium dimethoxytriphenylcarbinolcarboxylate*, $COOK\cdot C_6H_4\cdot C(C_6H_4\cdot OMe)_2\cdot OH$, which crystallises in needles, and is soluble in alcohol; when heated above 270°, it decomposes, and a *sublimate*, crystallising in yellow laminæ, melting at 148°, is obtained. On reducing the potassium salt with potash and zinc dust in alcoholic solution, and treating with hydrochloric acid, it gives *dimethoxytriphenylmethanecarboxylic acid*, $COOH\cdot C_6H_4\cdot CH(C_6H_4\cdot OMe)_2$, which crystallises in white needles melting at 149—150°, and is soluble in alkali carbonates, concentrated sulphuric acid, ether, benzene, chloroform, or carbon bisulphide. The *barium* salt crystallises in colourless needles containing $3H_2O$.

The *dibromo*-derivative of the dimethyl ether of phenolphthaleïn, $C_{22}H_{16}Br_2O_4$, is obtained by direct bromination, and crystallises in aggregates of colourless needles, melting at 160—161°. W. J. P.

**Derivatives of Phenolphthaleïn.** By GIORGIO ERRERA and E. BERTÈ (*Gazzetta*, 1896, **26**, i, 264—274).—Dinitrophenolphthaleïn (Hall, Proc., 1893, 14) can be readily obtained by cautiously dropping nitric acid into an alcoholic solution of phenolphthaleïn, and subsequently heating on the water bath; the nitro-compound separates on cooling, and crystallises in yellow needles, melting at 197°.

*Dibromodinitrophenolphthaleïn*,  $CO{<}\begin{smallmatrix}C_6H_4\\O\end{smallmatrix}{>}C[C_6H_2Br(NO_2)\cdot OH]_2$ $[C : NO_2 : OH : Br = 1 : 3 : 4 : 5]$, prepared by nitrating tetrabromophenolphthaleïn in a similar manner, crystallises in yellow prisms, melting at 235—236°, is sparingly soluble in the usual solvents, and is not acted on by hydroxylamine. Its *diacetyl* derivative is prepared by the ordinary methods, and forms an amorphous, yellow powder, melting at 145°; it differs from the parent substance in being insoluble in alkalis.

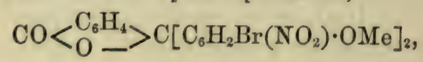
Dinitrophenolphthaleïn is reduced by tin and hydrochloric acid, but neither pure diamidophenolphthaleïn nor its hydrochloride could be isolated. Dibromodinitrophenolphthaleïn also readily undergoes reduction, and *dibromodiamidophenolphthaleïn hydrochloride*,



$$CO{<}\begin{smallmatrix}C_6H_4\\O\end{smallmatrix}{>}C[C_6H_2Br(NH_2)\cdot OH]_2,2HCl,$$

can be prepared from the product; it crystallises in minute, grey laminæ, decomposing on heating. The free *base* can be obtained as an amorphous, yellow powder, which is soluble in caustic alkalis, reacts with hydroxylamine, and gives a benzoyl derivative.

The *dimethyl* ether of dinitrophenolphthaleïn,



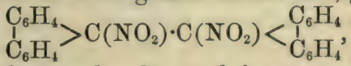
$$CO{<}\begin{smallmatrix}C_6H_4\\O\end{smallmatrix}{>}C[C_6H_2Br(NO_2)\cdot OMe]_2,$$

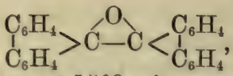
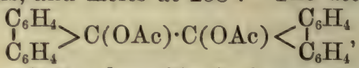
is obtained by heating the sodio- or argento-derivative of the phthaleïn with methylic iodide; it crystallises in short, yellow needles, melting at 130—132°, and is insoluble in alkalis or their carbonates. It is accompanied by the corresponding *monomethyl ether*, $C_{21}H_{14}N_2O_8$, which is a yellow, amorphous powder, melts at 90—92°, and dissolves readily in alkalis or alkali carbonates. On reducing the dimethyl ether with tin and hydrochloric acid, it yields the *dimethyl ether* of diamidophenolphthaleïn, $C_{22}H_{20}N_2O_8$, as a white, amorphous powder; when treated with nitrous acid, it is not converted into guaiacolphthaleïn, but into a *substance* of the composition $C_{22}H_{16}N_2O_{10}$. W. J. P.

**Introduction of a Fourth Radicle in place of the Hydroxyl Group of Triphenylcarbinol.** By KARL WEISSE (*Ber.*, 1896, **29**, 1402—1404).—Triphenylthienylmethane melts at 237°, not at 239° as previously stated (Abstr., 1895, i, 543). It is converted by bromine into a *monobromo*-derivative, which crystallises in long needles, and melts at 191—192°. It has not been found possible to bring about condensation between triphenylcarbinol and benzene, anisoïl, toluene, or naphthalene by the method employed with thiophen. Homologues of thiophen, on the other hand, undergo the reaction readily. *Methylthienyltriphenylmethane* melts at 181—182°, whilst *ethylthienyltriphenylmethane* melts at 111°. Monochlorothiophen also readily undergoes condensation, forming *chlorothienyltriphenylmethane*, which melts at 204—205°. The corresponding *iodo-compound* can also be readily obtained, and melts at 184—185°, whilst dibromo- and nitro-thiophen do not react. Thiophen, moreover, does not appear to react with trinitrotriphenylcarbinol.

A. H.

**Constitution of Colour Bases of the Triphenylmethane Series.** By HUGO WEIL (*Ber.*, 1896, **29**, 1541—1542).—The results of von Georgievics (this vol., i, 441) are not in accordance with those obtained by the author in a research which he is at present unable to complete. C. F. B.

**Bidiphenylenethylene and Bidiphenylenethane.** By CARL GRAEBE and H. STINDT (*Annalen*, 1896, **291**, 1—8; compare Abstr., 1893, i, 38, and this vol., i, 442).—The authors describe in some detail the method devised for the production of bidiphenylenethylene from fluorene and lead oxide (*loc. cit.*). Fusion with potash converts the red hydrocarbon into orthodiphenylcarboxylic acid, whilst hot, concentrated nitric acid, mixed with glacial acetic acid, gives rise to *dinitrobidiphenylenethane*,  $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}>C(NO_2)\cdot C(NO_2)<\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$, which crystallises in long, yellow needles, and melts, evolving gas, at 184—185°. The bromide of bidiphenylenethylene has been already described as yielding the red hydrocarbon on treatment with sodium, and bidiphenylenethane under the influence of alcoholic potash; the latter agent, if allowed to act during a sufficiently long period, also gives rise to the red hydrocarbon.

*Bidiphenylenethylene oxide*,  $\begin{array}{c}C_6H_4\\|\\C_6H_4\end{array}\!>C\overset{O}{\text{—}}C<\!\begin{array}{c}C_6H_4\\|\\C_6H_4\end{array}$, is obtained by heating the bromide with water at 150°; it separates from carbon tetrachloride in colourless crystals, and melts at 258°. The *acetate* of bidiphenylenethylene glycol,  $\begin{array}{c}C_6H_4\\|\\C_6H_4\end{array}\!>C(OAc)\cdot C(OAc)<\!\begin{array}{c}C_6H_4\\|\\C_6H_4\end{array}$, is produced on heating a solution of the bromide in benzene with silver acetate in a reflux apparatus; it separates from glacial acetic acid in colourless crystals, and melts, becoming red and decomposing, at 230°. The *glycol* is obtained on heating the acetate with baryta at 140°; it crystallises from alcohol in colourless needles, and melts at 237°.

The observation that bidiphenylenethane is the initial product of the action of heated lead oxide on fluorene, has led the authors to prepare the hydrocarbon in this manner, instead of by the action of sodium amalgam on the red hydrocarbon; it is also produced when fluorene and fluorenone are heated with sodium acetate at 310° and subsequently at 340—350°. Oxidation with sodium dichromate in glacial acetic acid gives rise to fluorenone. M. O. F.

**Formation of Dinitronaphthalenes. II.** By CH. GASSMANN (*Ber.*, 1896, **29**, 1521—1522; compare this vol., i, 486).—The formation of 1 : 4′- and 1 : 1′-dinitronaphthalene is evidently a function of the temperature, 1 : 1′-*dinitronaphthalene* is formed at the lowest possible temperature, especially at the commencement of nitration, and the yield is improved by allowing the reaction to proceed slowly. Heating towards the end of the reaction does not appear to improve the yield.

1 : 4′-*Dinitronaphthalene*, on the contrary, is best formed at a high temperature; the presence of concentrated acid is here of advantage. The author is still engaged in investigating the production of peri-dinitronaphthalene (*loc. cit.*). J. F. T.

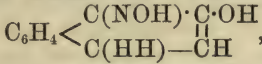
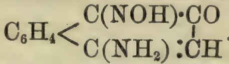
**Influence of Substituents on the Formation of Quinoximes.** By FRIEDRICH KEHRMANN and M. HERTZ (*Ber.*, **29**, 1415—1420).—The *oxime* of hydroxynaphthaquinoneimide, $C_{10}H_8N_2O_2$, exists in a red and yellow modification. The yellow modification crystallises from alcohol in bright yellow, silky needles, and melts and decomposes at about 200°; it dissolves very slowly in cold, dilute soda, forming a bright yellow solution, which on acidification with acetic acid, assumes a brick-red hue, and on subsequent evaporation, deposits the oxime in needles of that colour; the latter, unlike the yellow needles, dissolve quickly in dilute soda, and, when heated with water, dissolve, forming a red solution, which rapidly becomes yellow, and then deposits the yellow modification.

The oxime is reduced by a warm solution of stannous chloride in alcoholic hydrogen chloride, and the resulting colourless solution sets to a mass of needles, consisting of 1 : 4-diamido-2-naphthol *dihydrochloride*, $C_{10}H_5(NH_2)_2\cdot OH,2HCl$; the latter is obtained on passing hydrogen chloride into its aqueous solution in the form of beautiful, long, colourless needles, which on preservation become tinted superficially with violet; when warmed with acetic anhydride and anhydrous sodium acetate, it gives the *diacetyl* derivative, $C_{10}H_5(NHAc)_2 \cdot OH$, which possesses a marked phenolic character; this crystallises from acetic acid in colourless, granular crystals, and melts and decomposes at 250—260°. The ammoniacal solution of the hydrochloride is coloured by exposure to the atmosphere, the free base being thus oxidised. The product, 2 : 1 : 4-*hydroxynaphthaquinonediimide*, $C_{10}H_5(NH)_2 \cdot OH$, is precipitated in brownish-yellow needles; it is readily reduced to diamido-β-naphthol by stannous chloride, and dissolves in alcohol, forming a yellow solution, which, when warmed, becomes red, and on cooling deposits crystals of hydroxynaphthoquinoneimide; the latter is also produced from the diimide by the action of hot dilute hydrochloric acid.

2 : 4 : 1-*Amidonaphthaquinoneoxime*,

$$C_{10}H_5O(NH_2)(NOH)\ [NOH : NH_2 : O = 1 : 2 : 4],$$

is precipitated from alkaline solution by dilute acetic acid; it crystallises from alcohol in glistening yellow needles, and decomposes at 220—230°. It is reduced by means of stannous chloride to 1 : 2 : 4-amidodihydroxynaphthalene.

The existence of two modifications of hydroxynaphthaquinoneimide is best explained by assuming that the following formulæ represent the modifications stable in presence of alkali and acid respectively,  $C_6H_4\left<\begin{array}{l}C(NOH)\cdot C\cdot OH\\ C(HH)—CH\end{array}\right.$, and  $C_6H_4\left<\begin{array}{l}C(NOH)\cdot CO\\ C(NH_2):CH\end{array}\right.$. Analogous constitutions are suggested for Henrich's two modifications of nitroso-orcinol (this vol., i, 476).

A. L.

**Naphthalene-1 : 4′-dicarboxylic acid and its Derivatives.** By Pietro Moro (*Gazzetta*, 1896, **26**, i, 89—116).—1 : 4′-*Dicyanonaphthalene*, $C_{10}H_6(CN)_2$, is prepared from 1 : 4′-naphthalenediamine sulphate by carefully diazotising in hydrochloric acid solution, not allowing the temperature to rise above 0°, and converting the diazo-compound into the dicyano-derivative by the Sandmeyer reaction; it crystallises in white needles, melting at 266—267° (corr.), and is insoluble in water, but soluble in alcohol, ether, or acetic acid. On hydrolysis, preferably by prolonged boiling with alcoholic potash, but also by heating in a sealed tube with concentrated hydrochloric acid, or by treating with sulphuric acid, it is converted into *naphthalene-1 : 4′-dicarboxylic acid*; this is white and crystalline, and decomposes without melting at above 286°. The *ammonium* salt and the *calcium* salt, with $1H_2O$, crystallise in brownish prisms, whilst the *silver* salt forms a slightly coloured powder; the *barium* salt, with $3\frac{1}{2}H_2O$, crystallises in reddish prisms; the *methylic* salt in brownish laminæ, melting at 114—115° (corr.); and the *ethylic* salt in white needles, melting at 123—124° (corr.). The acid *chloride*, $C_{10}H_6(COCl)_2$, prepared by the action of phosphorus pentachloride on the acid, crystallises in white prisms, melting at 155—156° (corr.); on heating with phenol it yields the *diphenylic* salt, $C_{10}H_6(COOPh)_2$, which forms a crystalline mass, melting at 198—199° (corr.).

On heating the ammonium salt, it yields 1 : 4′-dicyanonaphthalene, and a *substance* which crystallises in white needles, decomposing above 240°, and seems to have either the constitution

$$NH(C_{10}H_6{\cdot}COOH)_2,$$

or $NH(CO{\cdot}C_{10}H_6{\cdot}COOH)_2$. The *silver* salt is a white crystalline powder, the *calcium* salt, with $3H_2O$, crystallises in yellow laminæ, and the *barium* salt forms yellow pyramids. The *amide* of the naphthalenedicarboxylic acid is obtained as a yellowish, amorphous powder, insoluble in the ordinary solvents, on boiling the acid chloride with ammonium carbonate solution.

*Trinitronaphthalene*-1 : 4′-*dicarboxylic acid*, $C_{10}H_3(NO_2)_3(COOH)_2$, may be prepared by direct nitration of the acid in presence of sulphuric acid, and is a yellow powder, soluble in ether, alcohol, or acetic acid; its *ethylic* salt crystallises in brown pyramids, melting at 152—153° (corr.), and the *barium* salt, with $2H_2O$, in brownish needles.

*Dinitronaphthalene*-1 : 4′-*dicarboxylic acid*, $C_{10}H_4(NO_2)_2(COOH)_2$ prepared by nitrating the carboxylic acid with boiling fuming nitric acid, is a yellow, crystalline powder; its *ethylic* salt crystallises in white laminæ, melting at 160°, with incipient decomposition, and the *methylic* salt in brown prisms, melting and decomposing at 210—215°. The *ammonium* salt could only be obtained as a resinous mass, and the *calcium* salt crystallises with $4\frac{1}{2}H_2O$ in yellow prisms.

On nitrating the amide with boiling fuming nitric acid, an *isomeride* of the above dinitronaphthalene-1 : 4′-dicarboxylic acid is obtained; it crystallises in yellow prisms, which decompose on heating, and gives a crystalline *ethylic* salt, melting at 253—254° (corr.) with decomposition.

Two *substances*, melting at 184—205° and at 157—165° respectively, are obtained by oxidising naphthalene-1 : 4′-dicarboxylic acid with potassium permanganate; these are still under investigation.

*Tetrahydronaphthalene*-1 : 4′-*dicarboxylic acid*, $C_{10}H_{10}(COOH)_2$, is prepared by reducing the naphthalenedicarboxylic acid with sodium amalgam; it crystallises in needles, melting at 237·5—238·5° (corr.), and decolorises alkaline permanganate in the cold. The *calcium* salt, with $3\frac{1}{2}H_2O$, and the *barium* salt, with $1H_2O$, crystallise in nearly white laminæ, but the ammonium, ethylic, and methylic salts could not be obtained in the crystalline form.

*Sulphonaphthalene*-1 : 4′-*dicarboxylic acid*, $C_{10}H_5(COOH)_2{\cdot}HSO_3$, is prepared by heating the dicarboxylic acid with sulphuric acid in closed tubes at 190—200°; it forms a crystalline, deliquescent, yellow mass, which begins to decompose at 275°, and yields a crystalline *barium* salt containing $2H_2O$. W. J. P.

**Isomeric Naphthalene Derivatives. III.** By Paul Friedländer and Hermann Rüdt (*Ber.*, 1896, **29**, 1609—1613; compare Abstr., 1895, i, 668).—1 : 3-*Amidonaphthol*-4-*sulphonic acid* is obtained by treating 1: 3-amidonaphthol with sulphuric acid at the ordinary temperature. The solutions of the alkali salts show a faint green fluorescence.

When it is heated with water or dilute sulphuric acid at 120°, it yields 1 : 3-*dihydroxynaphthalene* (naphtharesorcinol), which crystallises in lustrous plates, and melts at 124°. The *acetyl compound* melts at 56°. It is distinguished from the other isomerides by the fact that it forms naphthafluoresceïn (German Patent, 84,990), when heated with phthalic anhydride and zinc chloride. When treated in acetic acid solution with nitrosodimethylaniline, 1 : 3-dihydroxynaphthol is converted into a reddish-violet colouring matter. The azo-derivatives closely resemble those of resorcinol. When 1 : 3-dihydroxynaphthol is heated with aqueous soda at 180—190°, it is converted quantitatively into orthotoluic and acetic acids. It is less readily attacked by fused soda. When it is treated with ammonia or amines, the β-hydroxyl group is first attacked. Ammonia yields 3 : 1-amidonaphthol, together with a little 1 : 3-naphthylenediamine. Aniline converts it into *phenylamidonaphthol*, the alkaline solution of which rapidly absorbs oxygen from the air, with formation of naphthaquinonanil. 1 : 3-*Dihydroxynaphthol*-3′-*sulphonic acid* is obtained by heating the corresponding amidonaphtholsulphonic acid (German Patent, 82,676) with water at 120°; its *sodium salt* forms white needles. The azo-derivatives of this acid are yellow to yellowish-red. A. H.

**Unsaturated Sulphones of the Naphthalene Series.** By Julius Troeger and K. Artmann (*J. pr. Chem.*, 1896, [2], **53**, 484—500; compare Otto, Abstr., 1895, i, 229).—*β-Naphthylallylsulphone*, $C_3H_5{\cdot}SO_2{\cdot}C_{10}H_7$, is prepared by heating a β-naphthalenesulphinate with excess of allylic bromide in a reflux apparatus, distilling the excess of bromide, extracting the residue with water, and crystallising from alcohol; it forms long, white needles, melts at 95°, and dissolves in alcohol, ether, glacial acetic acid, benzene, and methylic alcohol, but not in water. When heated at 150° with water or aqueous alkali, the sulphone takes up a molecule of water, yielding the hydroxypropyl-β-naphthylsulphone described below. Nascent hydrogen is without action on the sulphone; bromine in glacial acetic acid converts it into the *dibromide*, $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}SO_2{\cdot}C_{10}H_7$, which crystallises in slender, white needles, melts at 85°, and dissolves in alcohol, ether, glacial acetic acid, and ethylic acetate, but not in water. When this dibromide is heated with water, it yields an *oxygen derivative*, $C_3H_5O{\cdot}SO_2{\cdot}C_{10}H_7$, which appears to be an anhydride of the corresponding glycol; it forms white crystals, and melts at 167°.

*β-Naphthylbromopropylsulphone* may be obtained by heating the sulphone with a saturated solution of hydrogen bromide in glacial acetic acid at 120°; it forms white, granular crystals, melts at 124°, and dissolves freely in alcohol and glacial acetic acid, sparingly in ether, but not in water. Water at 150° converts this bromo-derivative into the corresponding *β-naphthylhydroxypropylsulphone*,

$$OH{\cdot}CHMe{\cdot}CH_2{\cdot}SO_2{\cdot}C_{10}H_7,$$

which forms white, granular crystals, and melts at 137°. Alcoholic potash debrominates it, yielding the parent sulphone.

*β-Naphthyliodopropylsulphone* is analogously prepared, and crystallises in white needles, melting at 106°, and freely soluble in alcohol, glacial acetic acid, and ethylic acetate, sparingly in ether, and not in light petroleum; its behaviour in water is similar to that of the bromo-derivative.

*β-Dinaphthylpropylenedisulphone*, $C_{10}H_7 \cdot SO_2 \cdot CHMe \cdot CH_2 \cdot SO_2 \cdot C_{10}H_7$, from propylenic bromide and a β-naphthalenesulphinate, crystallises in lustrous, white laminæ, and melts at 123°.

*Trimethylene-β-dinaphthylsulphone*, $CH_2(CH_2 \cdot SO_2 \cdot C_{10}H_7)_2$, analogously prepared, is white, and melts at 145°.

*β-Trinaphthylallyltrisulphone*, $C_{10}H_7 \cdot SO_2 \cdot CH(CH_2 \cdot SO_2 \cdot C_{10}H_7)_2$, from allylic tribromide and a β-naphthalenesulphinate, is a white, flocculent substance, which melts at 230°, and is sparingly soluble; from the mother liquor of this compound, a white *sulphone* crystallises, which melts at 157°, and is also obtained by heating β-naphthylallylsulphone dibromide with a β-naphthalenesulphinate in alcoholic solution; the authors are disposed to regard this sulphone as a stereoisomeride of β-dinaphthylpropylenedisulphone, which has an asymmetric carbon atom (compare Otto, *loc. cit.*).

*β-Naphthylphenylpropylenedisulphone*, $SO_2Ph \cdot CHMe \cdot CH_2 \cdot SO_2 \cdot C_{10}H_7$, is prepared by heating a benzenesulphinate with β-naphthylallylsulphone dibromide in alcoholic solution; it crystallises in aggregates of needles, and melts at 123°. The behaviour of β-naphthylallylsulphone dibromide to β-naphthylhydrosulphide is described, the chief product being the *thio-ether*, $C_3H_5(SC_{10}H_7)_2 \cdot SO_2 \cdot C_{10}H_7$, which melts at 129°.

*Allyl-α-naphthylsulphone* crystallises in monoclinic prisms, and melts at 67°. A. G. B.

**Dianthranol.** By William R. Orndorff and C. L. Bliss (*Amer. Chem. J.*, 1896, **18**, 453—465).—A solution of anthranol in benzene was exposed to bright sunlight for some weeks, when the solution became successively dark green, yellow, and reddish-yellow, and white and reddish-yellow crystals separated, which were decolorised by bone-black, and purified by recrystallisation from acetone. The *dianthranol*, $C_{28}H_{20}O_2$, prepared in this way, crystallises in colourless, tabular, or columnar crystals, melts and decomposes at about 250°, and is very soluble in chloroform, less so in acetone, glacial acetic acid, and benzene, slightly soluble in alcohol, and almost insoluble in benzene. Solutions of the alkalis fail to dissolve dianthranol even when boiled, so that the compound may be separated from anthranol in this way. When a benzene solution of dianthranol is allowed to evaporate in air, partial oxidation to anthraquinone occurs. When heated in sulphuric acid at its melting point, dianthranol undergoes partial conversion into anthranol. The molecular weight of anthranol was determined by the cryoscopic method, and agreed with the formula $C_{14}H_{10}O$; the compound crystallises in the rhombic system, whilst dianthranol is monoclinic; crystallographical measurements of each are given.

Dianthranol is also formed when a solution of anthranol in benzene is boiled for 12 hours, and when air is passed through a solution of anthranol in potash. *Diacetyldianthranol* crystallises in light yellow plates, and melts and decomposes at 276—279°; it is very soluble in chloroform, and sparingly in benzene and alcohol. The authors consider that dianthranol consists of two molecules of anthranol, which are united by the broken para-linkings between the two γ-carbon atoms in each molecule (compare this vol., i, 176). A. G. B.

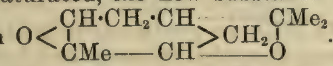
**Terpenes and Ethereal Oils.** By OTTO WALLACH (*Annalen*, 1896, **291**, 342—367).—I. [With G. M. KERR.]—Experimental details are now described respecting the neutral oxidation product of terpineol having the composition $C_{10}H_{16}O_3$ (Abstr., 1895, i, 547). The constitution of this substance, and its relation to terpenylic acid, have been already discussed (*loc. cit.*).

II. [With HENRY V. ARNY.]—The conversion of terpineol into carvone was first effected by obtaining carveol methyl ether from terpineol tetrabromide under the influence of sodium methoxide, and oxidising it with chromic anhydride (Abstr., 1895, i, 59). A more direct method is now described, terpineol nitrosochloride being converted into a hydroxy-oxime, which yields inactive carvone under the influence of dilute sulphuric acid.

*Hydroxydihydrocarvoxime*, $OH\cdot C_{10}H_{15}\!:\!NOH$, is obtained from terpineol nitrosochloride by the action of sodium ethoxide (1 mol.); it crystallises from ethylic alcohol, and melts at 133—134°. The *diacetyl* derivative crystallises from ethylic acetate, and melts at 107°. Dilute sulphuric acid converts hydroxydihydrocarvoxime into inactive carvone, and concentrated sulphuric acid gives rise to amidothymol (compare Abstr., 1894, i, 537).

III. [With RICHARD GUERICKE.]—The *dibromide* of pinole hydrate, 1 : 6 : 2 : 8-*dibromodihydroxyhexahydrocymene*, is prepared by adding a solution of bromine in chloroform to pinole hydrate in the same medium; it melts at 131—132°.

The *anhydride* of pinole glycol, $C_{10}H_{16}O_2$, is obtained by the action of sodium methoxide on the foregoing dibromide; whilst the latter is unsaturated, the new substance is saturated, and has the constitution

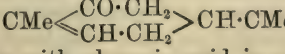


$O<\begin{array}{l}CH\cdot CH_2\cdot CH\text{---}\\ |\\ CMe\text{---}CH\text{---}\end{array}>CH_2\begin{array}{l}CMe_2\\ |\\ O\end{array}$

. The anhydride is an oil which boils at 206—207°, and at 82° under a pressure of 12 mm.; the sp. gr. = 1·0335 at 20°, and the refractive index, $n_D$ = 1·4588 at 20°. Hydrolysis converts the substance into pinole glycol, and it is, therefore, a true anhydride of that substance.

According to the view which regards pinole hydrate as an unsaturated substance containing two hydroxyl groups, of which one is united with a secondary and the other with a tertiary carbon atom, oxidation should give rise to a hydroxy-ketone.

*Hydroxydihydrocarvone*,



$CMe<\begin{array}{l}CO\cdot CH_2\\ CH\cdot CH_2\end{array}>CH\cdot CMe_2\cdot OH$

, is obtained by oxidising pinole hydrate with chromic acid in glacial acetic acid. The *semicarbazone* melts at 174°, and the *oxime* crystallises from ethylic alcohol, and melts at 134°.

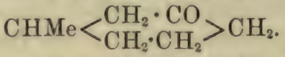
The original method of obtaining terpinolene from terpineol (Wallach and Kerkhoff, Abstr., 1893, i, 595) was modified by von

Baeyer (Abstr., 1894, i, 253). The author now prepares it with great facility by dissolving terpineol in anhydrous formic acid, and gently heating the liquid for a few minutes, when terpinolene rapidly separates.

It has been stated (Abstr., 1893, i, 595) that dipentene is produced when terpineol is heated at 180—190° with solid potassium hydrogen sulphate. The same result is effected in the presence of much water when the operation is performed at 250°, this temperature being maintained during six hours.

The author discusses the constitution of pinene, and criticises the conclusions at which Wagner has arrived (compare Abstr., 1894, i, 610). M. O. F.

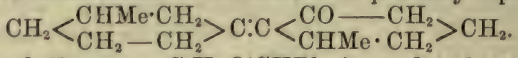
**Condensation Products of Cyclic Ketones: Syntheses in the Terpene Series.** By OTTO WALLACH (*Ber.*, 1896, **29**, 1595—1601).—The author has already shown (this vol., i, 309) that on hydrolysis, pulegone readily yields methylcyclohexenone,



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH_2}.$$

Subsequent investigation has shown that this substance lends itself to the synthesis of numerous compounds, the production of which depends on condensation.

The *bicyclic ketone*, $C_{14}H_{22}O$, is obtained in the form of the *hydrochloride*, $C_{14}H_{23}OCl$, melting at 90° when hydrogen chloride is led into methylhexenone, and the *hydrobromide*, $C_{14}H_{23}OBr$, which melts at 90—91°, is produced when hydrogen bromide is employed; the action of hot aniline on these compounds liberates the ketone, which boils at 143—144° under a pressure of 10 mm. The *oxime* melts at 120°, and yields, on reduction, the *base* $C_{14}H_{23}NH_2$, which melts at 50°, and boils at 165—166° under a pressure of 20 mm.; the *hydrochloride* and *platinochloride* are crystalline, and the *nitrate* is sparingly soluble in nitric acid. The constitution of the ketone is probably represented by the formula

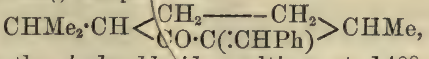


$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CHMe\cdot CH_2}\\ \mathrm{CH_2-CH_2}\end{matrix}{>}\mathrm{C{:}C}{<}\begin{matrix}\mathrm{CO-\!\!-CH_2}\\ \mathrm{CHMe\cdot CH_2}\end{matrix}{>}\mathrm{CH_2}.$$

*Benzylidenemethylhexenone*, $C_7H_{10}O{:}CHPh$, is produced on adding alcoholic sodium ethoxide to a mixture of methylhexenone and benzaldehyde (1 mol.), and is precipitated on adding water to the liquid; it crystallises from ether, and melts at 59°, boiling at 190—200° under a pressure of 13 mm. The *oxime* crystallises from dilute alcohol in colourless, transparent prisms, and melts at 109—110°.

*Dibenzylidenemethylhexenone*, $C_7H_8O(CHPh)_2$, is obtained by the same method as the foregoing substance, 2 mols. of benzaldehyde being employed; it crystallises from alcohol in small, intensely yellow needles, and melts at 126—128°.

Methylcyclohexenone also combines with other aldehydes, for example, nitrobenzaldehyde and cinnamaldehyde; with acetone it yields the *compound* $C_{10}H_{16}O$, which closely resembles pulegone, and is isomeric with it. The remarkable activity of methylhexenone most likely depends on the unsubstituted condition of the methylene group in juxtaposition to the carbonyl; and, on this assumption, the behaviour of cyclic ketones towards benzaldehyde presents a more convenient indication of their constitution than the production of hydroxymethylene derivatives. An investigation in this direction has given rise to the following compounds.

*Benzylidenementhone*,  $CHMe_2\cdot CH<\begin{matrix}CH_2\text{———}CH_2\\ CO\cdot C(:CHPh)\end{matrix}>CHMe$, is obtained in the form of the *hydrochloride* melting at 140°, when hydrogen chloride is led into a mixture of menthone and benzaldehyde (1 mol.); the compound boils at 188—189° under a pressure of 12 mm., and the *hydrobromide*, which is crystalline, melts and decomposes at 115—116°. The *oxime* is sparingly soluble in alcohol and ether, crystallising from these agents in woolly needles, which melt at 160—161°.

*Benzylidenepulegone* boils at 202—203°, under a pressure of 12 mm. Carvone also combines with benzaldehyde, yielding a solid condensation product.

*Benzylidene-eucarvone*, $C_{10}H_{12}O:CHPh$, separates in measurable crystals, and melts at 112—113°; along with it is produced a *compound*, which crystallises from a mixture of chloroform and alcohol in snow-white leaflets, and melts at 193—194°.

*Dibenzylidenesuberone*, $C_7H_8O(CHPh)_2$, separates from alcohol in colourless crystals, and melts at 107—108°.

*Dibenzylidenemethylpentenone*, $C_6H_6O(CHPh)_2$, is obtained from benzaldehyde (2 mols.) and β-methylketopentamethylene (Abstr., 1893, i, 130), and separates from alcohol in yellow crystals which melt at 149—151°. The methylpentenone also combines with acetone, and the *oxime* of the condensation product melts at 85—87°.

M. O. F.

**Root of Rumex Nepalensis (Wall.).** By OSWALD HESSE (*Annalen*, 1896, **291**, 305—312).—The astringent principle occurring in the root of *Rumex nepalensis* (Wall.), has been attributed to chrysophanic acid; the author having shown that chrysophanic acid obtained from *Parmelia parietina* differs from that derived from rhubarb, has studied the root in question, and isolated from it three new substances, one of which, rumicin, is isomeric with, and closely resembles, chrysophanic acid, but is not identical with it.

*Rumicin*, $C_{15}H_{10}O_4$, crystallises from light petroleum in golden-yellow leaflets with metallic lustre, and melts at 186—188°; the solution in caustic potash is purple-red, becoming colourless on exposure to carbonic anhydride, which precipitates rumicin. When heated with hydriodic acid, it yields chrysophanohydroanthrone, which is obtained from chrysophanic acid under the influence of the same agent (Abstr., 1895, i, 292).

*Nepalin*, $C_{17}H_{14}O_4$ (compare this vol., i, 315), crystallises from glacial acetic acid in microscopic, orange needles, and melts at 136°; it is insoluble in alkali carbonates, but dissolves in caustic potash, forming a purple solution, which becomes colourless under the influence of carbonic anhydride. The solution in concentrated sulphuric acid is blood-red. The *diacetyl* derivative crystallises from glacial acetic acid in lustrous, brownish-yellow rhombohedra, which darken at 170°, and melt at 181°.

*Nepodin*, $C_{18}H_{16}O_4$, crystallises from a mixture of benzene and light petroleum in long, greenish-yellow prisms, and melts at 158°. It dissolves readily in alkali carbonates, forming a yellowish-brown solution; the solution in concentrated sulphuric acid is an intense, yellowish-red colour. The *diacetyl* derivative crystallises in pale yellow rhombohedra, darkens at 180°, and melts and decomposes at 198°.

These three constituents of *Rumex nepalensis*, of which nepalin greatly preponderates, are separated from one another by extracting the root with ether, removing nepodin by means of aqueous potassium carbonate, evaporating the ether, and extracting the rumicin from the residue with boiling acetone; the nepalin remaining undissolved.

M. O. F.

**Chlorophyll.** By Edward Schunck and Leo Marchlewski (*Ber.*, 1896, **29**, 1347—1352).—Tschirch has recently (*Ber. deut. bot. Gesell.*, 1896, 76) questioned some of the authors' previous conclusions on this subject. They contest the accuracy of his results, and give an account of the present state of our knowledge of the chemistry of chlorophyll. By the action of hydrochloric acid, chlorophyll yields phylloxanthin, and this, by the further action of the acid, is converted into phyllocyanin; chlorophyll shows two absorption bands, phylloxanthin four, and phyllocyanin five. It has been found, not only in this case, but with all other chlorophyll derivatives, that the number of absorption bands increases as the chlorophyll complex is resolved. Tschirch regards phylloxanthin as a derivative of phyllocyanin; that this is incorrect is readily proved by shaking an ethereal solution of the former with hydrochloric acid, when it is quickly changed into the latter. The authors suggest that Tschirch's "phyllocyanic acid" is really impure phyllocyanin, as the absorption spectra are almost identical. "Phyllopurpuric acid," which he obtained by heating alkachlorophyll with alkali, is a mixture, one constituent being phylloporphyrin, $C_{16}H_{18}N_2O$, which is closely related to hæmatoporphyrin, $C_{16}H_{18}N_2O_3$, both in composition and in spectroscopic properties; these are best observed in ethereal, not in alcoholic, solution. An important step in the investigation of the constitution of chlorophyll was made when it was recognised as a pyrroline derivative.

J. B. T.

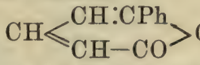
**Phenylcoumalin.** By J. A. Leben (*Ber.*, 1896, **29**, 1673—1680).—Phenylcoumalin is readily purified by Ciamician and Silber's method (Abstr., 1895, i, 554).—The best yield of the polymeric compound, $(C_{11}H_8O_2)_2$, is obtained by heating phenylcoumalin with concentrated hydrochloric acid at 110° during about 24 hours; the molecular weight was determined by the cryoscopic method in benzoic acid. No polymeride of phenyldimethylcoumalin could be prepared. δ-Phenylvaleric acid is formed by the reduction of phenylcoumalin by means of sodium amalgam, but hydriodic acid in acetic acid solution gives much better results. Phenylcoumalin forms additive compounds with various substances containing a phenylic group; they crystallise readily, but dissociate in solution. The *picric acid* and *salicylic acid* derivatives melt at 81—82° and 93° respectively. *Phenyldimethylcoumalin-quinol* crystallises in small, colourless needles, melting at 113°. *Phenylcoumalin-dianiline*, $C_{11}H_8O_2,2NH_2Ph$, crystallises with benzene in slender, colourless, stellate needles, melting at 115—118°; when dried, the compound becomes yellow; from alcohol, yellow nodular aggregates are deposited, melting at 142°. The yield is 70 per cent. of the phenylcoumalin employed.

When heated with concentrated hydrochloric acid, the aniline derivative yields 1 : 2-*diphenyl*-6-*pyridone*, crystallising in colourless, slender, reticular needles, melting at 144—146°.

2-*Phenyl*-6-*pyridone*, $C_{11}H_9ON$, is prepared by the interaction of phenylcoumalin and ammonium acetate; it crystallises in small, yellow plates, melting at 197°. The *hydrochloride* crystallises in small, pale yellow needles, melting at 104°; like the *aurochloride* and *platinochloride*, it is dissociated by water.

2-Phenylpyridine is formed by the distillation of the pyridone with zinc dust; the picrate melts at 175°, not at 169—172°, as stated by Skraup and Cobenzl; the *platinochloride* crystallises with $2H_2O$, in long, orange needles, melting at 204°. 2 : 6-*Phenylchloropyridine*, prepared by the action of phosphorus chloride on the pyridone at 150°, crystallises in colourless needles, melts at 34°, and is readily soluble in concentrated, but not in dilute, hydrochloric acid. The *aurochloride* crystallises in pale yellow needles.

These results confirm the formula,



$CH\Big<\begin{array}{l}CH{:}CPh\\CH-CO\end{array}\Big>O$

which Ciamician and Silber had previously suggested for phenylcoumalin; they show that Hesse's statements with regard to the purification of this compound are incorrect, and throw doubt on the existence of "oxyphenylcoumalin" which he has described. J. B. T.

**Synthesis of Carbazole.** By CARL GRAEBE and F. ULLMANN (*Annalen*, 1896, **291**, 16—17).—The action of nitrous acid on orthamidodiphenylamine converts it into phenylazimidobenzene, and when this substance is heated in a distilling flask at 360°, copious evolution of nitrogen occurs, and carbazole distils over almost free from phenylazimidobenzene. M. O. F.

**New Derivatives of Phenyldimethylpyrazolone.** By M. C. SCHUYTEN (*Chem. Centr.*, 1895, ii, 34; from *Maandbl. natuurw.*, **19**, 93—101).—*Phenyldimethylpyrazolone thiocyanate*, $C_{11}H_{12}N_2O,HSCN$, is best obtained by evaporating a solution of antipyrine and potassium thiocyanate in molecular proportions, and then adding concentrated hydrochloric acid; it crystallises in small, compact needles, which turn red when exposed to the air; melts at 121—122°, and is only sparingly soluble in cold water and ether, readily in hot water, alcohol, and benzene. When strongly heated, it decomposes, and yields obnoxious vapours. Its solutions give with ferric chloride a flocculent, red precipitate, consisting of *ferric phenyldimethylpyrazolone thiocyanate*, $(C_{11}H_{12}N_2O)_3Fe(SCN)_3$. This is readily soluble in alcohol, chloroform, and benzene, sparingly in water and ether.

*Phenyldimethylpyrazolone mercurochloride* of constant composition is only obtained when a moderately concentrated aqueous solution of antipyrine is poured into a solution of mercuric chloride. It forms a white, flocculent precipitate, melts at 150°, is only slightly soluble in hot water, is decomposed by concentrated acids, and gives a yellow precipitate of mercuric oxide with alkalis. With sodium peroxide, it yields metallic mercury. J. J. S.

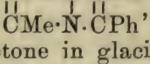
**Synthesis of Trimethylpyrazine and of Tetramethylpyrazine.** By P. Brandes and Carl Stoehr (*J. pr. Chem.*, 1896, [2], **53**, 501—512; compare Abstr., 1895, i, 569).—Tri- and tetra-methylpyrazine are formed when dimethylpyrazine methobromide is heated in a sealed tube at 270—280° for six hours; the product is fractionated, and the fractions are purified by conversion into their mercurochlorides. *Trimethylpyrazine*, $C_7H_{10}N_2$, is a colourless, highly refractive liquid; it does not solidify at 0°, and dissolves in water in every proportion, heat being developed; it boils at 171—172° (735 mm.), and is volatile in steam; its sp. gr. = 0·9958 at 0°/4° and 0·9787 at 18°/4°. In most of its compounds it behaves as a monacid base. The *normal aurochloride*, $C_7H_{10}N_2,HAuCl_4 + H_2O$, melts at 72°, or when anhydrous at 110°; it readily loses hydrochloric acid in water, passing into the *modified aurochloride*, $C_{10}H_7N_2,AuCl_3$, which melts at 137—138°. The *platinochlorides*, $(C_7H_{10}N_2)_2,HCl,PtCl_4$, $C_7H_{10}N_2,H_2PtCl_6 + 2\frac{1}{2}H_2O$, and $C_7H_{10}N_2,PtCl_4$ are described. The *mercurochloride*, $C_7H_{10}N_2,5HgCl_2$, forms sparingly soluble, lustrous, white, prismatic needles. The *picrate*, $C_7H_{10}N_2,2C_6H_3N_3O_7$, crystallises in lustrous, yellow, prismatic needles, and melts at 138—139°. The *methiodide*, $C_7H_{10}N_2,MeI$, crystallises in pale yellow, lustrous laminæ, decomposes at 231°, and is unusually soluble in water; a *periodide* is described. The *methochloride*, together with its *aurochloride*,

$$C_7H_{10}N_2,MeCl,AuCl_3$$

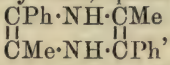
(m. p. 145°), its *mercurochloride*, $C_7H_{10}N_2,MeCl,6HgCl_2 + 2H_2O$ (m. p. 185°), its *platinochloride*, $C_7H_{10}N_2,Me_2PtCl_6$ were obtained. The base which Morin separated from fusel oil, and which boiled at 171—172° (Abstr., 1888, 572) was probably trimethylpyrazine.

*Tetramethylpyrazine*, $C_8H_{12}N_2$, has been described as dimethylketine (Abstr., 1881, 895), and has been obtained by Wolff (Abstr., 1887, 464) and Thal (Abstr., 1892, 1074); it crystallises in large, colourless, regular octahedra, melts at 86°, and boils at 189·5° (760 mm.). The *normal aurochloride*, $C_8H_{12}N_2,HAuCl_4 + 2H_2O$ (m. p. 173°), the *modified aurochloride*, $C_8H_{12}N_2,AuCl_3$ (m. p. 158°), the *picrate*, $C_8H_{12}N_2,2C_6H_3N_3O_7$ (m. p. 191—192°), and the *mercurochloride*, $C_8H_{12}N_2,6HgCl_2$ (m. p. 155—165°), are described. A. G. B.

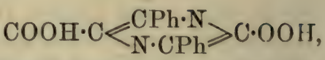
**Derivatives of Phenylacetone.** By Adalbert Kolb (*Annalen*, 1896, **291**, 253—297).—The action of ammonia on ω-bromacetophenone having led to the production of diphenylpyrazine, the behaviour of bromophenylacetone towards the agent has been studied.

3 : 6-*Diphenyldimethylpyrazine*, 
$\begin{matrix} CPh\cdot N\cdot CMe \\ \| \quad\ \ | \quad \| \\ CMe\cdot N\cdot CPh \end{matrix}$, is obtained by adding bromine to a solution of phenylacetone in glacial acetic acid, heating the liquid until colourless, pouring it upon ice, and treating the bromophenylacetone thus precipitated with alcoholic ammonia during

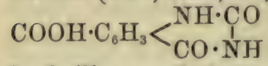
8—14 days; the alcohol is then removed by distillation, and the residue, after dilution with water, is extracted with ether and hydrochloric acid. Dimethyldiphenylpyrazine is deposited by the ether, and crystallises from ethylic acetate in small, colourless prisms; it sublimes very readily, and melts at 126°. The substance is also formed on reducing phenylacetoxime with tin and hydrochloric acid, and treating with soda the hydrochloride of the amido-ketone thus produced; the dioxime obtained by the action of hydroxylamine on phenylacetoxime yields the same product. The hydrochloric acid extract, to which reference has been made, contains the *base* $C_{32}H_{36}N_6$, which crystallises from alcohol in needles, and melts at 225°; the *hydrochloride* melts at 234—235°, the *sulphate* crystallises in needles, the *picrate* melts at 165—166°, and the *chromate* crystallises in small, red needles. The *mercurochloride* crystallises in needles, and the *platinochloride* forms reddish-yellow, rhombic prisms, blackens at 220°, and melts at 228°; the *aurochloride* separates in rhombic crystals, and melts at 165—166°.

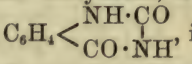
The alcoholic mother liquor of diphenyldimethylpyrazine deposits a mixture of two bases, which may be separated by means of their different solubility in benzene. The more sparingly soluble *base*, $C_9H_9NO$, crystallises from benzene in plates, and melts at 89—90°; its *platinochloride* crystallises in yellow, quadratic leaflets. 3 : 6-*Diphenyldimethyldihydropyrazine*,  $\begin{matrix}\mathrm{CPh{\cdot}NH{\cdot}CMe}\\ \| \qquad\qquad \| \\ \mathrm{CMe{\cdot}NH{\cdot}CPh}\end{matrix}$, is the base which dissolves more readily in benzene, and crystallises from alcohol in yellowish plates melting at 102°; the *hydrochloride* crystallises in silky needles, and melts at 104—106°, solidifying at the latter temperature, and melting finally at 180—186°. The *mercurochloride* crystallises from water in long needles, and the *platinochloride* separates from alcohol in reddish-yellow, rhombic prisms; the *aurochloride* crystallises from alcohol in reddish-yellow needles, and melts at 144—145°.

*Phenylacetoxime*, NOH:CPh·COMe, is prepared by slowly adding phenylacetone to a well-cooled mixture of amylic nitrite and alcoholic sodium ethoxide, and extracting the liquid repeatedly with ether; treatment of the aqueous solution of the sodium derivative with acetic acid precipitates the ketoxime, which crystallises from the glacial acid in needles, whilst the ethereal extract deposits a *compound*, $C_{34}H_{30}O_4$, which crystallises from alcohol in small needles, and melts and decomposes at 209°. The *acetyl* derivative of phenylacetoxime crystallises from dilute alcohol in plates, and melts at 61—62°; the *benzyl* derivative, which dissolves very readily in all agents excepting petroleum, melts at 62°. As already stated, reduction of phenylacetoxime gives rise to an amido-ketone; the *hydrochloride*, $C_9H_{11}NO,HCl$, sinters at 200°, and becomes red and melts at 208°. The aqueous solution reduces cold Fehling's solution, and also mercuric chloride in presence of caustic soda; treatment with hot caustic alkali liberates benzaldehyde and ammonia. The *platinochloride* crystallises in dark red, six-sided prisms, and melts and decomposes at 215°.

3 : 6-*Diphenylpyrazinedicarboxylic acid*,  $\mathrm{COOH{\cdot}C}<\begin{matrix}\mathrm{CPh{\cdot}N}\\ \mathrm{N{\cdot}CPh}\end{matrix}>\mathrm{C{\cdot}OOH}$, is produced when diphenyldimethylpyrazine is treated during 20—24 hours with a boiling 2 per cent. solution of potassium permanganate; it is very readily soluble in alcohol, crystallises from hot water in beautiful needles, and melts at 190°. The *ammonium* and *potassium* salts are very soluble in water, and the *silver* salt crystallises in small white needles; the *ethylic* salt crystallises from dilute alcohol in small needles, and melts at 104°. When diphenylpyrazinedicarboxylic acid is heated with glacial acetic acid in sealed tubes at 150—180°, carbonic anhydride is eliminated, and Staedel's isoindole is produced.

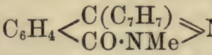
The action of hydroxylamine on phenylacetoxime gives rise to the dioxime $C_9H_{10}N_2O_2$, melting at 239—240°, which Müller and von Pechmann obtained from phenyl methyl diketone and hydroxylamine (Abstr., 1889, 1170); along with it is produced a *compound*, $C_{27}H_{27}N_3O_7$, which melts at 117—118°. The *benzyl* derivative of the dioxime dissolves with difficulty in petroleum, and melts at 155°; the *dibenzyl* derivative crystallises from petroleum in large needles, and melts at 55—56°. M. O. F.

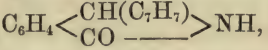
**Oxidation of Quinazoline Derivatives.** By STEFAN NIEMENTOWSKI (*Ber.*, 1896, **29**, 1356—1361).—*Uramidobenzoylcarboxylic acid*,  $\mathrm{COOH{\cdot}C_6H_3}<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{CO{\cdot}NH}\end{matrix}$ [COOH : NH : CO = 1 : 3 : 4], is prepared by boiling methyluramidobenzoyl with potassium permanganate in alkaline solution; in acid solution, at the ordinary temperature, the yield is smaller. Methyluramidobenzoyl is very stable towards chromic anhydride in glacial acetic acid solution, and the portion attacked is completely oxidised to carbonic anhydride. The acid is practically insoluble, except in alkalis, aniline, &c.; it readily forms gummy, colloïdal, yellow aggregates, decomposes at about 405°, and appears to contain $1{\cdot}5H_2O$. The *ammonium* salt exhibits, in moderately dilute solution, an intense blue fluorescence; the *silver* salt is colourless and flocculent.

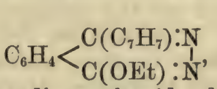
4′-*Hydroxyquinazoline chromate*, $C_8H_6N_2O,CrO_3$, crystallises in pomegranate-coloured quadratic plates, chars at about 200°, and is extremely stable towards chromic anhydride. When oxidised by means of chromic anhydride, 4′-hydroxyquinazoline yields orthouramidobenzoyl,  $\mathrm{C_6H_4}<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{CO{\cdot}NH}\end{matrix}$, in very small quantity.

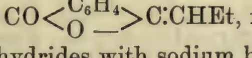
2′-*Methyl-4′-hydroxyquinazoline hydrochloride*, $C_9H_8N_2O,HCl$, crystallises in colourless plates or slender needles, and decomposes at 336°; the *nitrate* crystallises in colourless needles melting at 195°; the *chromate* forms yellow, nodular masses, decomposes suddenly at 182°, and becomes dark brown when exposed to direct sunlight. The base is not oxidised by boiling nitric acid; potassium permanganate in alkaline solution attacks only a small portion, which is converted into carbonic anhydride. J. B. T.

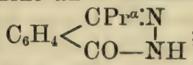
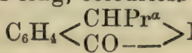
**Phthalazine Derivatives.** By OTTO BROMBERG (*Ber.*, 1896, **29**, 1434—1442; compare Gabriel and Neumann, Abstr., 1893, i, 346).—The best method of preparing benzylphthalazone is to heat benzylidene phthalide and hydrazine with dilute alcohol in sealed tubes at 100°; the yield is quantitative.

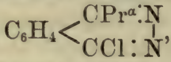
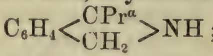
1′ : 3′-*Benzylmethylphthalazone*,  $C_6H_4{<}\substack{C(C_7H_7)\\ CO\cdot NMe}{>}N$, is formed when benzylphthalazone, dissolved in dilute alcohol, is mixed with excess of methylic iodide; it is insoluble in water and hydrochloric acid, and crystallises from methylic or ethylic alcohol in shining crystals melting at 148°. 1 : 3-*Benzylethylphthalazone*, $C_{17}H_{16}ON_2$, crystallises from methylic alcohol in white crystals, which become yellow on exposure to air; it is insoluble in hydrochloric acid, and melts at 106°.

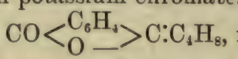
1′-*Benzylphthalimidine*,  $C_6H_4{<}\substack{CH(C_7H_7)\\ CO\ \text{———}}{>}NH$, obtained on reducing 1-benzylphthalazone by means of zinc and acetic acid, forms stellate groups of needles, melts at 137°, and dissolves readily in alcohol, benzene, acetic acid, and strong hydrochloric acid. When warmed with phosphorus oxychloride, it gives a carmine red solution. It appears to be identical with the substance obtained on reducing benzylphthalimide with hydriodic acid.

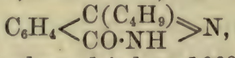
4′ : 1′-*Ethoxybenzylphthalazine*,  $C_6H_4{<}\substack{C(C_7H_7){:}N\\ C(OEt){:}N}$, formed by acting on benzylchlorophthalazine with sodium ethoxide, dissolves readily in nearly all the ordinary solvents, but is sparingly soluble in water, and is practically insoluble in petroleum; it is deposited from alcohol in crystals, and melts at 84—86°. 4′ : 1′-*Phenoxybenzylphthalazine*, $C_{21}H_{16}ON_2$, produced by a similar reaction, crystallises from alcohol in cube-like crystals, and melts at 155°; its solution in hydrochloric acid gives a precipitate with platinum chloride. Attempts to produce derivatives of isoindole and dihydroisoindole by reducing benzylchlorophthalazine proved unsuccessful.

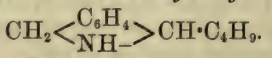
*Propylidenephthalide*,  $CO{<}\substack{C_6H_4\\ O\ \text{—}}{>}C{:}CHEt$, is prepared by heating phthalic and butyric anhydrides with sodium butyrate at 175° during eight hours; it forms a viscid, clear yellow oil, which solidifies to a mass of slender, white needles in a freezing mixture, but regains its fluidity at ordinary temperatures; it boils at 169—170° under 12 mm. pressure. It dissolves in potash, subsequent addition of hydrochloric acid causing the precipitation of *butyrophenoneorthocarboxylic acid*, $COPr^a\cdot C_6H_4\cdot COOH$; the latter dissolves in ether and ethylic acetate, and crystallises from a mixture of ethylic acetate and petroleum in groups of colourless needles melting at 89°.

Propylidinephthalide and hydrazine unite in alkaline solution, with production of 1-*propylphthalazone*,  $C_6H_4{<}\substack{CPr^a{:}N\\ CO\text{—}NH}$; the latter is insoluble in water, but dissolves in hydrochloric acid, and crystallises from alcohol in long, colourless needles, melting at 156°. 1′-*Propylphthalimidine*,  $C_6H_4{<}\substack{CHPr^a\\ CO\ \text{——}}{>}NH$, is produced by the reduction of the foregoing substance; it crystallises from hot water in white needles, melting at 135—136°, and is soluble in ether.

4′:1′-*Chloropropylphthalazine*,  $C_6H_4<\begin{array}{l}CPr^{a}{:}N\\ CCl{:}N\end{array}$, is readily prepared by acting on propylphthalazone with phosphorus oxychloride at 100°; it crystallises from dilute alcohol in colourless needles melting at 67°. It dissolves readily in warm dilute hydrochloric acid, and the resulting solution yields precipitates on addition of platinum and gold chlorides, potassium ferrocyanide, and dichromate. When reduced by means of zinc and hydrochloric acid, it yields a base which proves to be 1′-*propyldihydroisoindole*,  $C_6H_4<\begin{array}{c}CPr^{a}\\ CH_2\end{array}>NH$; this decomposes on exposure to air, and has an odour resembling piperidine. The *hydrochloride*, $C_{11}H_{15}N,HCl$, melts at 203°; its solution gives precipitates with platinum and gold chlorides, picric acid and potassium ferrocyanide, but not with potassium chromate.

*Isobutylidenephthalide*,  $CO<\begin{array}{c}C_6H_4\\ O—\end{array}>C{:}C_4H_8$, is prepared by heating isovaleric anhydride, phthalic anhydride, and sodium isovalerate at 220° during five hours. It forms large crystals, and dissolves readily in hot alkalis and all the ordinary solvents with the exception of light petroleum. It crystallises from benzene or amylic alcohol in light yellow, isolated crystals, which melt at 97°. *Isovalerophenoneorthocarboxylic acid*, $C_4H_9\cdot CO\cdot C_6H_4\cdot COOH$, is obtained in the form of its potassium salt when the foregoing substance is heated with aqueous potash; it crystallises from a mixture of ethylic acetate and light petroleum in needles, and, when dried, melts at 88°.

1′-*Isobutylphthalazone*,  $C_6H_4<\begin{array}{c}C(C_4H_9)\\ CO\cdot NH\end{array}>N$, crystallises from alcohol in white crystals, and, when dried at 100°, melts at 113°. 4′ : 1′-*Chlorisobutylphthalazine*, prepared from the latter by the action of phosphorus oxychloride, forms a clear syrup, which dissolves in hydrochloric acid without giving a crystalline hydrochloride; it affords, however, a crystalline *picrate*, $C_{12}H_{13}N_2Cl,C_6H_3N_3O_7$, and a *platinochloride*, $(C_{12}H_{13}N_2Cl),H_2PtCl_6$, the former being a bright yellow substance which crystallises from alcohol, and melts at 122°, the latter melting at 216°. The foregoing base, when reduced by zinc and hydrochloric acid, yields another, which is oily and does not give crystalline salts; the *platinochloride*, however, is crystalline, and on analysis proves to have the composition $(C_{12}H_{17}N)_2,H_2PtCl_6$, and is therefore probably derived from *isobutyldihydroisoindole*,



$$CH_2<\begin{array}{c}C_6H_4\\ NH—\end{array}>CH\cdot C_4H_9.$$

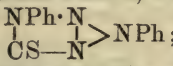
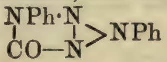
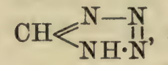
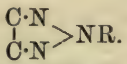
A. L.

**Constitution of Safranines.** By Rudolf Nietzki (*Ber.*, 1896, **29**, 1442—1446).—The author objects to some of the conclusions of O. Fischer and Hepp (this vol., i, 323), and to the nomenclature proposed by Jaubert (*ibid.*, 325). He has obtained the same mauveïne from metamidodiphenylamine and paramidodiphenylamine, and from diphenylmetaphenylenediamine and paraphenylenediamine; had the condensation taken place unsymmetrically, different substances would have been obtained, so it is inferred that the safranines have symmetrical formulæ.

The azonium formula is to be preferred to the quinoneimide one, on account of the marked basic character of the safranines; diacetylsafranine, for example, in spite of its two acetyl groups, is still a strong base. C. F. B.

**Action of Nitrous acid on Diphenylthiosemicarbazide and Diphenylsemicarbazide.** By MAX BUSCH and JULIUS BECKER (*Ber.*, 1896, **29**, 1686—1691).—Diphenylthiosemicarbazide,

$$NHPh\cdot CS\cdot NH\cdot NHPh,$$

is readily prepared by heating phenylthiocarbazinic acid with aniline, hydrogen sulphide being eliminated; the reaction appears to be a general one for primary and secondary amines. By the action of nitrous acid the carbazide probably yields a nitroso-derivative, $NO\cdot NPh\cdot CS\cdot NH\cdot NHPh$, which changes spontaneously into the cyclic compound,  $\begin{matrix}NPh\cdot N\\ |\qquad |\\ CS—N\end{matrix}\!>\!NPh$; by the further action of nitrous acid, sulphur is eliminated, the compound being oxidised to 1 : 3-*diphenylisotetrazolone*,  $\begin{matrix}NPh\cdot N\\ |\qquad |\\ CO—N\end{matrix}\!>\!NPh$; this contains a complex isomeric with Bladin's tetrazole,  $CH\!<\!\begin{matrix}N—N\\ \qquad \|\\ NH\cdot N\end{matrix}$, and resembles in constitution Zincke's pseudoazimido-derivatives,  $\begin{matrix}C\cdot N\\ |\\ C\cdot N\end{matrix}\!>\!NR$. It crystallises in dark red needles, melts and decomposes at 110°, and, in acid solution, dyes silk golden orange, the colour being stable. The yield is quantitative, and the molecular weight, determined by the cryoscopic method in phenolic solution, agrees with the formula. The salts are yellow and stable in presence of free acid at the ordinary temperature, but when boiled, they yield phenylazocarbonanilide (see below). The isotetrazolones are not changed by alkalis; they differ from the tetrazolones in colour and basicity. The *hydrochloride* crystallises in lemon coloured needles melting at 164°; the *sulphate*, $C_{13}H_{10}ON_4,H_2SO_4$, *picrate*, and *platinochloride*, $C_{13}H_{10}ON_4,H_2PtCl_6$, crystallise in yellow needles melting at 188°, 133—134°, and 218° respectively; the *nitrate* also crystallises in slender, golden needles. Diphenylsemicarbazide is formed by the reduction of the isotetrazolone by means of zinc dust and acetic acid, showing that the phenyl group retains its original position.

*Nitrosodiphenylsemicarbazide*, $NO\cdot NPh\cdot CO\cdot NH\cdot NHPh$, prepared from diphenylsemicarbazide and nitrous acid, crystallises in slender needles, melts at 174—175°, quickly decomposes in moist air, and gives Liebermann's reaction. When warmed with alcohol, phenylazocarbonanilide is formed, and all attempts to prepare the diphenylisotetrazolone were unsuccessful.

*Phenylazocarbonanilide*, $NPh\!:\!N\cdot CO\cdot NHPh$, prepared in the manner described above, is also formed when diphenylsemicarbazide is oxidised by means of ferric chloride; it crystallises in lustrous, orange-red plates, melts at 121—122°, gives no nitroso-derivative, and is not changed by acids or alkali. J. B. T.

**Ketones of the Tropine Group. III. Tropinone and Nortropinone.** By RICHARD WILLSTÄTTER (*Ber.*, 1896, **29**, 1575—1584; compare this vol., 327).—When tropinone hydrochloride is treated with potassium cyanide in aqueous solution, *tropinonecyanhydrin*, $C_9H_{14}N_2$, is formed. It crystallises in long, colourless, lustrous prisms, and melts and decomposes into its constituents at 145°. *α-Ecgonine* is formed by the hydrolysis of this compound, and is a very hygroscopic neutral substance. It will shortly be more fully described.

Tropigenine can readily be purified by recrystallisation from ether followed by conversion into the *carbamate*, which melts and decomposes at 166°. n-*Benzoyltropigenine*, $C_7H_{12}ONBz$, crystallises in milk-white aggregates of slender prisms, and melts at 125°. It is less soluble in water at 50—60° than in either cold or boiling water. When tropigenine carbamate is treated with chromic acid, it is converted into *nortropinone*, $C_7H_{11}NO$, which crystallises in thin, colourless needles and plates, melting at 69—70°. This substance closely resembles tropinone in its properties. The *carbamate* is a snow-white, hygroscopic mass. The *hydrochloride* is very hygroscopic, and melts and decomposes at 201°. The *platinochloride* decomposes above 200°, the *aurochloride* melts and decomposes at 168°, and the *picrate* melts at 158—160°.

*Nitrosonortropinone* crystallises in yellowish needles, melts indefinitely at about 127°, and shows Liebermann's reaction faintly. *Nortropinonoxime*, $C_7H_{11}N\colon NOH$, is sparingly soluble in cold water, crystallises in thin, rhomboidal plates, and melts at 181—182°. n-*Benzoylnortropinonoxime*, $C_7H_{10}NBz\colon NOH$, melts at 175°.

A. H.

**Bases from the Cell-nucleus.** By ALBRECHT C. L. M. L. KOSSEL (*Zeit. physiol. Chem.*, 1896, **22**, 176—187).—Protamine is a substance originally prepared by Miescher from the spermatozoa of the salmon. Piccard attributed to it the formula $C_{16}H_{31}N_9O_4$.

In the present research it was prepared both from salmon and sturgeon sperm. The sulphate from salmon sperm has the formula $C_{16}H_{31}N_9O_3,H_2SO_4$. That from sturgeon sperm has rather different solubilities in sodium chloride solutions, and the names *salmine* and *sturine* are suggested by the two protamines. By decomposing the latter base with sulphuric acid, a new crystalline base was prepared, which is called *histidine;* its *hydrochloride*, which forms large, colourless, rhombic crystals $[a : b : c = 0{\cdot}76665 : 1 : 1{\cdot}71104]$, has the formula $C_{12}H_{20}N_6O_4,2HCl + 2H_2O$ or $C_6H_9N_3O_2,HCl + H_2O$. Among the other decomposition products, arginine was obtained, but little or no amido-acids. The protamines give the biuret, but not Millon's, reaction. W. D. H.

**Formation of Ethylic Cholate.** By LASSAR COHN (*Zeit. physiol. Chem.*, 1896, **22**, 196).—The author now confirms Vahlen's statement (this vol., i, 453) that ethylic cholate is not formed when pure cholic acid is boiled with alcohol. The impure acid employed in his earlier observations contained hydrochloric acid, which acted as an etherifying agent.

**Behaviour of Paracaseïn with Rennet.** By OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1896, **22**, 103—126).—The term paracaseïn is used for caseïn which has been acted on by rennet; the term caseïn being used synonymously with caseïnogen.

The statement originally made by the author and unanimously adopted that caseïn differs from caseïnogen in that the latter is, whilst the former is not, curdled by rennin *plus* calcium salts has been recently questioned by Peters (*Preisschrift. Rostock*, 1894). Peters alleges that when caseïn is dissolved in lime water, and Witte's "Labessenz" added, a precipitation occurs. This is not, however, due to the action of the enzyme, but is produced by the large amount of sodium chloride present in the preparation used; the calcium compound of caseïn is very readily precipitated by sodium chloride, especially at 40°. W. D. H.

*Note by Abstractor.*—Practically the same conclusion was arrived at by Edmunds (this vol., ii, 489), who, however, was unable to obtain Witte's preparation. He was inclined to attribute the action rather to calcium salts than to sodium salts in the essence. W. D. H.

**Optical Behaviour of some Vegetable Proteïds.** By JOHAN GUSTAV CHRISTOPHE THORSAGER KJELDAHL (*Bied. Centr.*, 1896, **25**, 197—199; from *Forhandl. skand. Naturfors.*, 1892, 385—390).—The amount of proteïds extracted from wheat meal by dilute alcohol varies according to the strength of the alcohol (minimum with 20 per cent., maximum with 55 per cent., alcohol), but is not influenced by the amount of alcohol, by the length of time, and only slightly by the temperature. In the author's experiments 55 per cent. alcohol was employed at the ordinary temperature. The proteïds were precipitated by cooling with freezing mixtures, being several times redissolved and precipitated by cooling. Finally they were precipitated with a large amount of absolute alcohol, treated with ether, and dried in a vacuum. All the preparations showed an almost constant percentage of carbon (about 52·0 per cent.) and nitrogen (17·25 per cent.), and a rotatory power, in 55 per cent. alcohol, of $[\alpha]_D = -92°$, Ritthausen supposed that wheat meal contains three proteïds soluble in alcohol, but the above results indicate the presence of only one.

The rotatory power of acetic acid solutions depends on the strength of the acid. With glacial acid $[\alpha]_D = -81°$; with 5 to 0·1 per cent. $[\alpha]_D = -111°$. Solutions in very dilute caustic alkali solutions gave the same result as dilute acetic acid. With solution in phenol at 40° $[\alpha]_D = -130°$.

The solubility of the proteïds of rye meal resembled that of wheat meal. C = 53·6, N = 17·20 per cent. $[\alpha]_D$ in 55 per cent. alcohol $= -121°$, in dilute acids $= -144°$, in glacial acetic acid $= -105°$, and in phenol $= -157°$.

The proteïds of barley meal again showed similar solubility.

C = 53·0, N = 16·52 per cent. The rotatory power of the different solutions was less constant than in the case of wheat and rye. The average results were: In 55 per cent. alcohol $[\alpha]_D = -111°$, in dilute acetic acid $= -130°$, and in phenol $= -149°$.

In the case of oat meal, the greatest solubility was in 60 per cent. alcohol, which, however, did not dissolve much, and the soluble compound readily changes to an insoluble modification. Alcoholic solutions could not be got clear enough for polarisation. In dilute acetic acid or caustic soda $[\alpha]_D = -83°$ (?).

With maize meal, the minimum solubility was with 40 to 50 per cent., the maximum with 75 to 85 per cent., alcohol; and the proteïds have to be precipitated with water. $[\alpha]_D = -35°$ in 75 per cent. alcohol and $-28°$ in glacial acetic acid. Dilute acetic acid solutions are completely precipitated by sodium chloride. On the other hand, the solvent power of dilute alcohol is increased by addition of sodium or calcium chlorides, and the rotatory power seems to be slightly raised by such addition. N. H. J. M.

**Colour Reactions of Proteïds with Nitrous acid and Phenols.** By KARL LANDSTEINER (*Chem. Centr.*, 1895, ii, 891; from *Centr. Physiol.*, **9**, 433—434; compare this vol., ii, 284).—The author shows that his former statement that no diazo-compound results from the action of nitrous acid on proteïds is incorrect.

The compound obtained on treating salicylic acid with nitrous acid is a *diazosalicylic acid*, $C_7H_4O_3N_2$, which, when warmed with hydriodic acid, yields a colourless, crystalline, iodine compound. From a solution of sodium salicylate, which had been treated with sodium nitrite and hydrochloric acid, the author obtained a small quantity of a substance crystallising in needles; its reactions with brucine and diphenylamine proved it to be a nitrate, and the results of analysis agreed roughly with those required for diazophenol nitrate.

J. J. S.

**Compounds of the Colouring Matter of the Blood with Heavy Metals.** By JOAN JUTT (*Chem. Centr.*, 1895, ii, 683; from *Pharm. Zeit. Russ.*, **34**, 503—505).—Oxyhæmoglobin obtained from any particular species of animal, is a well-defined compound; that obtained from horse's blood has the composition C = 54·5, H = 7·25, N = 17·51, S = 0·449, F = 0·393, and O = 19·85 per cent., corresponding with the formula $C_{648}H_{1040}N_{178}S_2FO_{177}$.

Oxyhæmoglobin readily forms compounds with salts and double salts of the heavy metals; the compounds thus obtained are very sparingly soluble in blood, especially in the presence of sodium chloride. On this basis, the author has constructed a method for the volumetric estimation of the colouring matter in blood by means of zinc and copper salts. The metallic compounds are obtained by the replacement of five hydrogen atoms in oxyhæmoglobin by five atoms of a metal, the valency of the metal appearing to be without influence. The main action of heavy metals as poisons is that the formation of the metallic compounds with the oxyhæmoglobin renders the blood incapable of acting as an oxygen carrier. J. J. S.

# Organic Chemistry.

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**Preparation of Cyanogen Bromide, Bromonitromethane, and Dibromonitromethane.** By ROLAND SCHOLL (*Ber.*, 1896, **29**, 1822—1825).—In order to avoid the separation of insoluble bye-products on adding bromine to a concentrated solution of potassium cyanide, the author has modified the preparation of cyanogen bromide in the following manner. A solution of 65 grams of potassium cyanide in 120 grams of water, cooled to 0°, is slowly added to 150 grams of bromine, maintained at the temperature of melting ice, the liquid being agitated during the operation; the yellow product is heated at 65—70° in a retort, when 90 per cent. of the calculated amount of cyanogen bromide distils over. The crystalline substance which separates during the action, is probably a double compound of potassium bromide and cyanogen bromide; it is decomposed at the temperature subsequently attained.

Tscherniak's method of preparing mono- or dibromonitromethane consists in adding an aqueous solution of the sodium derivative of nitro- or bromonitro-methane to the calculated quantity of bromine. By excluding water, however, the author has succeeded in considerably improving the yield of these substances; the sodium derivative is added to the theoretical amount of bromine dissolved in carbon bisulphide, sodium bromide being then removed by agitation with water, and excess of the halogen by treatment with sulphurous acid.

M. O. F.

**Action of Acetylene on Iron, Nickel, and Cobalt reduced by Hydrogen.** By HENRI MOISSAN and CHARLES MOUREU (*Compt. rend.*, 1896, **122**, 1240—1243).—Acetylene acts readily at the ordinary temperature on iron, nickel, and cobalt if they have been reduced from their oxides at the lowest possible temperature. There is great development of heat, and, if the current of gas is rapid, the metal becomes incandescent. Part of the acetylene is converted into benzene and other polymerides, but the greater part splits up into carbon and hydrogen.

It would seem that the phenomena are due to the energetic absorption of the gas by the porous reduced metal; heat is thus developed, part of the acetylene is polymerised, and part is decomposed. As soon as decomposition begins, the reserve energy of the acetylene becomes available and contributes to the energy of the reaction. Carefully prepared spongy platinum produces a similar decomposition. On the other hand, if the acetylene is diluted with nitrogen, there is no incandescence, though the acetylene is absorbed and slightly decomposed.

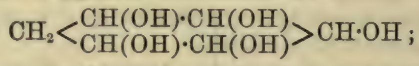
If the metals have been heated at too high a temperature during the process of reduction, heat is necessary in order to start the decomposition of the acetylene.

C. H. B.

**Preparation of Methylic Nitrate.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1895, [3], **13**, 1044—1045).—The author recommends the following modified form of Champion's method for the preparation of methylic nitrate: 50 c.c. of concentrated sulphuric acid are slowly added to 150 c.c. of methylic alcohol (98—99 per cent.), care being taken that the temperature does not rise too much. This mixture is then gradually poured into a previously prepared mixture of 100 c.c. of concentrated sulphuric acid and 150 c.c. of pure nitric acid (36°), which is kept at a temperature of 12—14°. 100 c.c. of concentrated sulphuric acid is then added, and the whole quickly agitated by means of a glass ring; the temperature rises to 20°, and in a few minutes all the ethereal salt separates. The yield is good.

J. J. S.

**Quercitol.** By HEINRICH KILIANI and J. SCHÄFER (*Ber.*, 1896, **29**, 1762—1766).—The molecular refractive power of quercitol, and the production of benzene when it is reduced by means of hydriodic acid, led Kanonnikoff to suggest that its formula is



$$CH_2<\begin{matrix}CH(OH)\cdot CH(OH)\\ CH(OH)\cdot CH(OH)\end{matrix}>CH\cdot OH;$$

if this is correct, it should yield malonic acid when oxidised by means of potassium permanganate; this is found to be the case. The quercitol (1 part) is dissolved in water (100 parts) and mixed at the ordinary temperature with potassium permanganate (4 parts), dissolved in water (120 parts). The malonic acid was identified by means of the calcium and barium salts. In addition to malonic acid, the oxidation products are oxalic acid, carbonic anhydride, an acid, in very small quantity, probably isomeric with malic acid, and, in considerable quantity, a compound which readily reduces alkaline copper solution. These results prove that quercitol contains a $CH_2$ group, which, by the action of concentrated nitric acid, is attacked in two ways, since Kiliani and Scheibler have previously shown, that in these circumstances it yields mucic acid and trihydroxyglutaric acid.

By the action of bromine water on quercitol, a diketone, $C_6H_8O_5$, is probably formed, but its separation from bromo-derivatives, which are simultaneously produced, is extremely difficult; at the ordinary temperature it yields an *osazone*, $C_{18}H_{20}O_3N_4$, crystallising in yellow or yellowish-red aggregates of needles, softening at 170°, and melting and decomposing at about 180°.

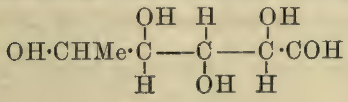
The removal of the excess of bromine and of hydrogen bromide in cases such as the above, where bromine water has been employed as an oxidising agent, is conveniently accomplished by shaking the liquid with successive portions of silver oxide; this is more convenient than passing a current of carbonic anhydride through the liquid and heating it.

J. B. T.

**Ammoniacal Derivatives of Mannose, of Sorbose, and of Galactose.** By CORNELIS A. LOBRY DE BRUYN, and FREDERICK H. VAN LEENT (*Rec. Trav. Chim.*, 1896, **15**, 81—83; compare Abstr., 1896, i, 118).—When an ammoniacal solution of mannose in methylic alcohol is evaporated in a vacuum and then treated with a little dry ether, an amorphous substance, which gradually becomes crystalline, separates; this melts and decomposes at about 158°, and has the composition $C_{12}H_{23}O_{10}N$, being formed from 2 mols. of mannose and 1 mol. of ammonia by the loss of 1 mol. of water. Its specific rotatory power, $[\alpha]_D = -28{\cdot}3°$, and, when boiled with an acid and then neutralised with alkali, it yields mannose.

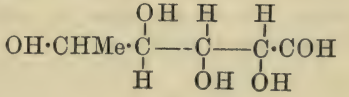
*Sorbosamine*, $C_6H_{13}NO_4$, was obtained by treating an ammoniacal solution of sorbose in methylic alcohol which had been evaporated in a vacuum, with dry ether. The quantity obtained was too small to be completely investigated. When galactosamine (*loc. cit.*) is boiled with absolute methylic alcohol, and ether is added, a hygroscopic crystalline deposit is formed having the same composition as the above-mentioned ammoniacal derivative of mannose; it is formed by the elimination of a molecule of ammonia from 2 mols. of glucosamine.
J. J. S.

**Isorhamnose.** By EMIL FISCHER and HEINRICH HERBORN (*Ber.*, 1896, **29**, 1961—1967).—The well-known method of inducing intramolecular change in acids of the sugar group by means of hot pyridine, has been applied to rhamnonic acid, which is thus converted into isorhamnonic acid; reduction of the lactone with sodium amalgam gives rise to isorhamnose, which has the configuration I, rhamnose being represented by the expression II.



$$\mathrm{OH{\cdot}CHMe{\cdot}}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{\cdot}COH}$$

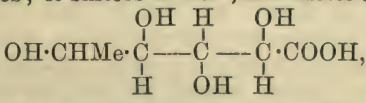
I.



$$\mathrm{OH{\cdot}CHMe{\cdot}}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\mathrm{{\cdot}COH}$$

II.

Rhamnonic acid is prepared by oxidising rhamnose with bromine water; the lactone dissolves in acetone with some difficulty, 100 parts being required for 3·85 parts of the substance at 20°. The *brucine* salt dissolves in three parts of boiling alcohol, and crystallises in long, colourless needles; it sinters at 120°, and melts at 126°.

*Isorhamnonic acid*,  $\mathrm{OH{\cdot}CHMe{\cdot}}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{\cdot}COOH}$, is obtained by dissolving 200 grams of rhamnolactone in 1 litre of water, and heating it in autoclaves with 170 grams of pyridine for three hours at 150—155°; it is separated from the product by means of the *brucine* salt, which crystallises in lustrous needles, and melts at 165°. The *lactone* separates from ethylic acetate in colourless crystals, and melts at 150—152°, becoming brown at 190—200°; it dissolves very readily in water, and, being in part converted into the acid, exhibits very rapid alteration of specific rotatory power, which falls from −62·02° to −46° in 20 minutes, and becomes constant at −5·21° if heated during 24 hours. The *phenylhydrazide* crystallises from alcohol in slender needles, and dissolves with difficulty in acetone; it sinters at 148°, and melts at 152°.

When isorhamnolactone is oxidised with dilute nitric acid, inactive xylotrihydroxyglutaric acid is formed, identical with the substance obtained from xylose (Fischer and Piloty, Abstr., 1892, i, 440); rhamnose and rhamnonic acid, when oxidised in this manner, yield the lævorotatory acid.

*Isorhamnose* is obtained by reducing the lactone with $2\frac{1}{2}$ per cent. sodium amalgam. The *phenylhydrazone* is very readily soluble, and the osazone is identical with rhamnosazone; the *ethyl mercaptal* crystallises from ether, and melts at 97—98° (corr.). Boiling dilute hydrochloric acid converts isorhamnose into δ-methylfurfuraldehyde (compare Fischer and Liebermann, Abstr., 1894, i, 4), and the sugar combines with hydrogen cyanide, forming the nitrile of a dicarboxylic acid. M. O. F.

**Transformation of Sugars by means of Lead Hydroxide.** By Cornelis A. Lobry de Bruyn and W. Alberda van Ekenstein (*Rec. Trav. Chim.*, 1896, **15**, 92—96).—In consequence of the recent publication by Svobodo (this vol., i, 406) of his researches on the action of basic lead acetate solutions on different sugars, the authors are obliged to publish their work on the transformation of sugars by means of lead hydroxide. The products obtained by the action of this reagent differ somewhat from those formed by the action of potash, soda, or lime (this vol., i, 116). Glucose when heated with lead hydroxide yields mannose, but no fructose; fructose although transformed yields neither glucose nor mannose as it does with potash. Mannose, also, is not at all, or only very slightly, transformed into fructose.

A comparative table, showing the action of lead hydroxide and potash on glucose, mannose, fructose, and galactose, is given. This contains the specific rotatory power after transformation, the amount of the transformed material destroyed by boiling with hydrochloric acid and the specific rotatory power of the residue. J. J. S.

**New Hydrazones of Sugars. Naphthylhydrazones and Alkylated Phenylhydrazones.** By W. Alberda van Ekenstein and Cornelis A. Lobry de Bruyn (*Rec. Trav. Chim.*, 1896, **15**, 97—99).—The authors have prepared the unsymmetrical naphthylhydrazones, also the α-ethyl-, α-amyl-, α-allyl-, and α-benzyl-hydrazones of various sugars, namely glucose, galactose, mannose, arabinose, rhamnose, xylose, and lactose. Many of these hydrazones will, probably, be of use in separating mixtures of sugars, on account of their different solubilities, &c. Fructose yields no crystalline compound with any of the hydrazines mentioned.

A detailed account of the properties of these hydrazones will shortly appear. J. J. S.

**Methylamines.** By Marcel Delépine (*Compt. rend.*, 1896, **122**, 1272—1274; compare this vol., i, 519).—Methylamine hydrochloride melts indistinctly at about 210°, dimethylamine hydrochloride forms long prisms which melt sharply at 171°, and trimethylamine hydrochloride melts at about 271—275°, a temperature much higher than that stated by Cambier and Brochet.

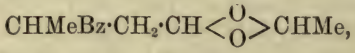
The picrates of the methylamines, unlike the hydrochlorides, are only slightly soluble, are not deliquescent, and have somewhat well defined melting points. The salts of methylamine and dimethylamine can be obtained by the direct action of picric acid on the methylic compounds previously described (*loc. cit.*). *Methylamine picrate* forms large rhombic crystals which melt at 207° (uncorr.) and dissolve in 75 parts of water at 11°; *dimethylamine picrate* forms flattened rhombic crystals which melt at 155—156° (uncorr.) and dissolve in 56 parts of water at 11°; *trimethylamine picrate* crystallises in small needles which melt at 216° (uncorr.), and dissolve in 77 parts of water at 11°. The methylamine salt is orange-yellow, the trimethylamine salt lemon-yellow, whilst the colour of the dimethylamine salt is intermediate.

With iodine in presence of an alkali, trimethylamine readily yields the compound $Me_3NI_2$ which melts at 66°, whilst a solution of iodine in an alkali iodide added to a salt of trimethylamine gives a green crystalline precipitate of the compound $Me_3NI,HI_4$, already described by Weiss; it melts at 65°. The other two amines give no similar precipitate.

Nessler's reagent with di- and trimethylamine gives a white precipitate, soluble in water, but with methylamine it forms a pale yellow precipitate insoluble in water or an excess of the reagent. It has the composition $Me_2N_2,3HgI,\frac{1}{2}Hg + H_2O$. C. H. B.

**The Reaction of Triethylphosphine with Oxygen.** By W. P. Jorissen (*Ber.*, 1896, **29**, 1707—1709).—When triethylphosphine is exposed to air in the absence of water, it always absorbs rather more oxygen than is necessary for the formation of triethylphosphine oxide, $POEt_3$, a small amount of the ethereal salt of phosphinic acid being also formed. In the presence of water, on the other hand, the amount of oxygen is exactly that calculated for the formation of the oxide. When the absorption takes place in the presence of a substance such as indigo, which is not attacked by ordinary oxygen, the colouring matter is rapidly oxidised, and the absorption of oxygen is exactly doubled. A. H.

**Action of Sodium on Acetaldehyde.** By Paul C. Freer (*Amer. Chem. J.*, 1896, **18**, 552—562).—Acetaldehyde reacts violently with sodium so that dilution with ether and cooling are imperative; hydrogen is evolved and a white crystalline sodium compound, believed to be $CH_2\vdots CH\cdot ONa$, separates, but polymerises to a brown substance before it can be analysed. When a mixture of benzoic chloride and aldehyde is run into a flask containing sodium covered by ether, hydrogen is evolved and sodium chloride separates; if the ethereal solution is washed with water and dilute potash, to remove benzoic acid, dried over sodium sulphate, and evaporated in a vacuum, the residual oil yields white crystals. This compound has the formula $C_{13}H_{16}O_4$, melts at 86—87°, and dissolves in alcohol, benzene, and chloroform, but not in water. When heated with water at 100°, it yields benzoic acid, aldol, and aldehyde; when destructively distilled, or heated with dilute hydrochloric acid, it is converted into benzoic acid, crotonaldehyde, and acetaldehyde; when warmed with alkalis it dissolves, and aldehyde resin is formed. From the behaviour of the compound as described above, the author concludes that the substance is *aldehydoaldol benzoate*,



$$\mathrm{CHMeBz{\cdot}CH_2{\cdot}CH{<}\genfrac{}{}{0pt}{}{O}{O}{>}CHMe},$$

sodium acetaldehyde being first formed during the preparation, and then undergoing condensation which stops at aldol if benzoic chloride is present, but otherwise proceeds further.

The mother liquor of the aldehydoaldol benzoate proved to be aldol benzoate, for it behaved on distillation identically with a similar syrup prepared from aldol, sodium, and benzoic chloride.

A. G. B.

**Condensation Products of Isobutaldehyde.** By G. URBAIN (*Bull. Soc. Chim.*, 1895, [3], **13**, 1048—1052).—If isobutaldehyde is treated with its own weight of a 5 per cent. alcoholic solution of soda, a vigorous action takes place, and the product, after the evaporation of the alcohol, yields, on distillation at 15 mm. pressure, three fractions, (1) to 110°, (2) from 110—150°, (3) above 150°. The first fraction on further distillation at atmospheric pressure yields a compound boiling at 140°, and identical with that previously obtained by Fossek (Abstr., 1882, 161) on heating the aldehyde with sodium acetate solutions in sealed tubes. Its composition is represented by the formula $\mathrm{CMe_2{:}CH{\cdot}CMe_2{\cdot}CHO}$.

The second fraction yields a compound which boils at 125—130° under a pressure of 14 mm. This has the composition $C_8H_{16}O_2$, and is identical with Fossek's diisobutaldehyde (*loc. cit.*). Treated with acetic chloride it yields a *monacetyl* derivative which boils at 230—235°, and when reduced in ethereal solution with sodium it yields a crystalline compound, $C_8H_{18}O_2$, identical with the glycol, $\mathrm{CHMe_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CHMe_2}$, obtained by Fossek on treating isobutyraldehyde with alcoholic potash. Fossek's diisobutaldehyde is therefore *dimethyl*-2 : 5-*hexaneol*-3-*one*-4,

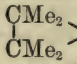
$$\mathrm{CHMe_2{\cdot}CH(OH){\cdot}CO{\cdot}CHMe_2}.$$

Its *oxime* boils at 133—135° under a pressure of 13 mm. The third fraction is still under investigation. If, when the soda is added to the isobutaldehyde, care is taken that no rise in temperature occurs and that the soda is neutralised by means of carbonic anhydride before evaporating off the alcohol, a colourless oil, which boils at 95° under a pressure of 14 mm. is obtained. This is *trimethyl*-2 : 2 : 4-*pentane-ol*-3-*al*-1, $\mathrm{CHMe_2{\cdot}CH(OH){\cdot}CMe_2{\cdot}CHO}$. The yield is poor as it is readily acted on by alkalis and converted into trimethylpenteneal and dimethylhexanediol. When treated with acetic anhydride in sealed tubes, it yields a *monacetyl* derivative which boils at 200—210°, and when reduced yields the glycol,

$$\mathrm{CHMe_2{\cdot}CH(OH){\cdot}CMe_2{\cdot}CH_2{\cdot}OH},$$

which forms a *diacetyl* derivative, boiling at 110—115°.

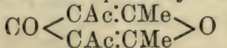
J. J. S.

**Hydrogenation of Pinacoline.** By MAURICE DELACRE (*Compt. rend.*, 1896, **122**, 1202—1205).—The author considers that the general adoption of the formula, $CMe_3\cdot COMe$, for pinacoline, in preference to the formula,  $\left.\begin{array}{l}CMe_2\\ |\\ CMe_2\end{array}\right>O$, is not supported by any decisive evidence, and is to be traced (1) to the failure of all attempts to hydrogenise pinacoline and (2) to the analogies which must necessarily exist between the two functions represented by the formulæ, these analogies not yet having been clearly defined and differentiated.

Concentrated hydrobromic acid acts readily on pinacoline, and yields a compound of the composition $C_6H_{12}Br_2$. When heated with alcoholic potash, this product gives the same yield of the same hydrocarbon of the ethylene series as the pinacone bromide obtained by the same method. When reduced with zinc and acetic acid, both bromides give the same yield of tetramethylethylene. Further, pinacoline bromide, when heated in a sealed tube with alcoholic potash, yields no trace of acetylene. It follows that both pinacone and pinacoline bromides are symmetrical.

The other products of the action of hydrogen bromide on pinacoline and pinacone, are bipropenyl, very small quantities of pinacoline or an isomeride, and resinous products. With hydrochloric acid in place of hydrobromic acid, the quantity of the haloïd derivative obtained diminishes. With hydrochloric acid and pinacone, the yields are very similar to those obtained with hydrobromic acid and pinacoline; with hydrochloric acid and pinacoline, the latter simply dissolves and becomes brown, but no resinous products are formed.

It follows from these results that pinacoline can be hydrogenised indirectly; its exact constitution is still uncertain. C. H. B.

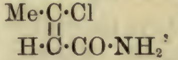
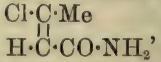
**Action of Carbonyl Chloride on Dithioacetylacetone.** By VICTOR VAILLANT (*Bull. Soc. Chim.*, 1895, [3], **13**, 1094—1095; compare Abstr., 1895, i, 168).—A benzene solution of dithioacetylacetone, $C_{10}H_{14}S_2O_4$, was treated with an excess of carbonyl chloride, also dissolved in benzene, and the mixture kept for about two months; after evaporation, it yielded a small quantity of Thomas and Lefevre's dimethyldiacetylpyrone,  $CO<\begin{array}{l}CAc:CMe\\ CAc:CMe\end{array}>O$ (Abstr., 1889, 235).

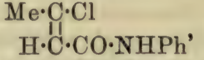
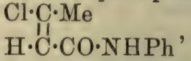
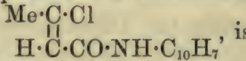
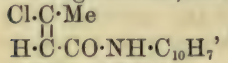
J. J. S.

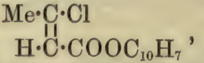
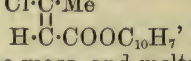
**Magnesium Nitride.** By OSKAR EMMERLING (*Ber.*, 1896, **29**, 1635).—Magnesium nitride, although violently attacked by water, is not affected by acidyl chlorides or by alcohol and ethylic iodide at 200°. When, however, it is treated with cold acetic anhydride, heat is developed, and the product, when fractionally distilled, yields some quantity of an oil, boiling at 80--82°, which proves to be acetonitrile; in like manner, when treated with benzoic anhydride it yields benzonitrile. A. L.

**New Derivatives of the Isomeric $\beta$-Chlorocrotonic acids.** By WILHELM AUTENRIETH (*Ber.*, 1896, **29**, 1665—1670).—The acidyl chlorine atom of the isomeric $\beta$-chlorocrotonic chlorides is readily replaceable by amido-, acidyl-, and phenoxy-groups, and in all the following instances the isomerism of the acids is represented in the compounds produced.

β-Chlorisocrotonic chloride distils without alteration, whilst β-chlorocrotonic chloride, under these conditions, undergoes complete isomeric change with production of the former compound.

*β-Chlorisocrotonamide*,  $\begin{matrix}\mathrm{Me\cdot C\cdot Cl}\\ \|\\ \mathrm{H\cdot C\cdot CO\cdot NH_2}\end{matrix}$, produced by the interaction of the corresponding chloride and aqueous ammonia, dissolves readily in alcohol, ether, chloroform, and hot water, and separates from the last two in pearly leaflets, melting at 109—110°. It is not altered by boiling with dilute mineral acids, but is partially decomposed by hot alkalis, hydrogen chloride being eliminated. It dissolves in 86 parts of water at 15°. *β-Chlorocrotonamide*,  $\begin{matrix}\mathrm{Cl\cdot C\cdot Me}\\ \|\\ \mathrm{H\cdot C\cdot CO\cdot NH_2}\end{matrix}$, dissolves readily in alcohol, ether, and chloroform; 22 parts of water at 15° dissolve 1 part of the amide. It crystallises from water in beautiful, transparent prisms or dull needles, and melts at 99—101°. When heated at 150—160°, it is carbonised.

*β-Chlorisocrotonanilide*,  $\begin{matrix}\mathrm{Me\cdot C\cdot Cl}\\ \|\\ \mathrm{H\cdot C\cdot CO\cdot NHPh}\end{matrix}$, is best prepared by the Baumann-Schotten reaction; it dissolves readily in alcohol and ether, but is insoluble in water; it crystallises from alcohol in flat, shining needles, and melts sharply at 106°; it has feebly basic properties, being dissolved by concentrated hydrochloric acid and reprecipitated on addition of water. *β-Chlorocrotonanilide*,  $\begin{matrix}\mathrm{Cl\cdot C\cdot Me}\\ \|\\ \mathrm{H\cdot C\cdot CO\cdot NHPh}\end{matrix}$, is similar in properties to the isomeric anilide; it crystallises from alcohol in fine prisms and melts at 123—124°. *β-Chlorisocrotonic-α-naphthylamide*,  $\begin{matrix}\mathrm{Me\cdot C\cdot Cl}\\ \|\\ \mathrm{H\cdot C\cdot CO\cdot NH\cdot C_{10}H_7}\end{matrix}$, is readily soluble in alcohol and ether, but is insoluble in water; it crystallises from alcohol in flat, shining needles, and melts at 155°. *β-Chlorocrotonic-α-naphthylamide*,  $\begin{matrix}\mathrm{Cl\cdot C\cdot Me}\\ \|\\ \mathrm{H\cdot C\cdot CO\cdot NH\cdot C_{10}H_7}\end{matrix}$, crystallises from alcohol in fine prisms, and melts at 169—170°.

*β-Naphthylic β-isochlorocrotonate*,  $\begin{matrix}\mathrm{Me\cdot C\cdot Cl}\\ \|\\ \mathrm{H\cdot C\cdot COOC_{10}H_7}\end{matrix}$, prepared by the action of the chloride on the sodium compound of β-naphthol, is insoluble in water, but dissolves readily in alcohol and ether; it crystallises from alcohol in white, shining leaflets, and melts at 67°. *β-Naphthylic β-chlorocrotonate*,  $\begin{matrix}\mathrm{Cl\cdot C\cdot Me}\\ \|\\ \mathrm{H\cdot C\cdot COOC_{10}H_7}\end{matrix}$, separates from alcohol as an indistinctly crystalline mass, and melts at 99—100°.

A. L.

**Rapic acid.** By JULIUS ZELLNER (*Monatsh.*, 1896, **17**, 309—313).—Rapic acid, prepared by Reimer and Will's prescription (Abstr., 1887, 1030), was treated with phosphorus triiodide, and the iodo-acid thus produced was hydrogenised by zinc and hydrochloric acid, whereby stearic acid was obtained. This formation of stearic acid renders it unlikely that rapic acid has the formula $C_{18}H_{34}O_3$, which was assigned to it by Reimer and Will; for since it cannot be acetylised, and is not, therefore, a hydroxy-acid, it is not conceivable how one of the oxygen atoms can be eliminated by iodine. New analyses of zinc rapate confirm the author's view that the formula for this acid is $C_{18}H_{34}O_2$; the acid is not identical with oleïc acid, since it does not give the elaïdin reaction. A. G. B.

**Tautomerism of Ethylic Acetoacetate.** By ISIDOR TRAUBE (*Ber.*, 1896, **29**, 1715—1723).—The tautomeric forms of ethylic formylphenylacetate (Wislicenus, this vol., i, 552) behave in a remarkable manner to solvents. When the α- or hydroxyl-form is dissolved in alcohol, the density of the solution gradually increases for some time after the solution has been prepared. This appears to be due to the gradual passage of a portion of the compound into the β- or keto-modification. That such a change actually takes place is shown by the fact that the reaction given by the α-form with ferric chloride is much more intense in chloroform solution than in alcoholic solution. The β-form gives no coloration with ferric chloride. The author has found that ethylic acetoacetate also behaves in a similar manner with certain solvents. In this case, the reaction with ferric chloride, which is characteristic of the hydroxyl form, is most strongly marked in methylic alcohol, and becomes gradually less strong in the following solvents: ethylic alcohol, amylic alcohol, water, pyridine, and glycerol, dark red; acetone, light red; methylic acetate, light pink; ethylic acetate, ethylic ether, and paraldehyde, faint pink; methylal, benzene, chloroform, carbon bisulphide, and carbon tetrachloride, colourless. According to this, therefore, the solution in alcohol contains almost entirely the hydroxyl form, whilst that in chloroform contains the keto-form. It is also to be observed that the coloration in those solvents which favour the production of the hydroxyl form gradually increases, so that equilibrium between the two forms present is not reached at once.

Similar conclusions may be drawn from the density of the solutions. The hydroxyl form has the smaller molecular volume, and it is found that the solutions in methylic and ethylic alcohols gradually increase in density for some time after their preparation, whilst, on the other hand, those in benzene and ethylic acetate decrease. The results point to the fact that the aqueous solution contains more of the hydroxyl form than of the keto-form.

When a few drops of ferric chloride are added to ethylic acetoacetate, the solution becomes much more intensely coloured when it is heated, whilst, if it be cooled in solid carbonic acid and ether, the colour entirely disappears. This, therefore, shows that the keto-form is most stable at low temperatures, and is converted into the hydroxyl form by rise of temperature. A. H.

**Formation of Additive Products from the Sodium Compounds of Ethylic Formylacetate and Acetoacetate, and Nitroethane.** By ARTHUR MICHAEL (*Ber.*, 1896, **29**, 1794—1799).

—The author holds the view that in an action such as that of ethylic sodioformylacetate on phenylic isocyanate the sodium first unites with the carbonyl oxygen, and that subsequently the two free carbon bonds in the residues $CHO{\cdot}\dot{C}H{\cdot}COOEt$ and $NPh{:}\dot{C}{\cdot}ONa$ unite. Similarly, the formation of nitromethaneazobenzene is not a case of substitution, but of addition of sodium to the most negative of the unsaturated nitrogen atoms of the diazo-salt, whereby a carbon and nitrogen bond are set free and reciprocally saturate one another; the sodium is subsequently eliminated as sodium chloride. A similar example is that of the reaction between sodium phenoxide and amylic nitrite (Walker, Abstr., 1884, 1003). The author extends this view to all cases of substitution in which an oxygenated radicle replaces a hydrogen atom combined with carbon. Numerous instances are cited in support of these views. A. R. L.

**Derivatives of Alkylic Cyanacetates.** By J. GUINCHANT (*Compt. rend.*, 1896, **122**, 1209—1212).—When alkylic sodiocyanacetates act on an equivalent quantity of an acid chloride in presence of dry ether, a new series of compounds is formed. Their composition is equivalent to the sum of a molecule of acetocyanacetate and a molecule of cyanacetate, and the author provisionally terms them *acetylbicyanacetates;* they have a feeble acidic function, but do not decompose alkali carbonates.

*Methylic acetylbicyanacetate*, $C_{10}H_{12}O_5N_2$, melts at 101°, and its aqueous or alcoholic solution gives, with a trace of alkali, a beautiful, golden-yellow coloration, which fades after a time in the cold, and immediately on heating. With potassium hydroxide, a salt of a new acid is obtained, which melts at 240°.

*Ethylic acetylbicyanacetate* melts at 83° and crystallises from alcohol in large, monoclinic tables with six faces; *pm*, 96° 30′; *mm*, 122° 45′; *pa*$_1$, 49° 20′.

It is possible that, in the formation of these compounds, an aldol reaction takes place between the ketonic oxygen of the acetocyanacetate and the hydrogen attached to the same carbon as the carboxylic group of the cyanacetate;

$$COOR{\cdot}CH(CN){\cdot}CMe{:}O + H{\cdot}CH(COOR){\cdot}CN = COOR{\cdot}CH(CN){\cdot}CMe(OH){\cdot}CH(COOR){\cdot}CN.$$

Claisen has explained in the same way the formation of an analogous compound in the interaction between acetone, ethylic oxalate, and sodium. The same explanation would follow if it were assumed that ethylic acetocyanacetate is capable of existing in an enolic form, $OH{\cdot}CMe{:}C(CN){\cdot}COOR$. C. H. B.

**Action of Isobutaldehyde on Malonic and Cyanacetic acids.** By LUDWIG BRAUN (*Monatsh.*, 1896, **17**, 207—224).—The method of synthesising unsaturated acids by the condensation of malonic acid with acetaldehyde and propaldehyde has not been applied to the production of higher homologues. The author has therefore heated malonic acid with isobutaldehyde and glacial acetic acid containing 10 per cent. of the anhydride at 100° in a reflux apparatus, obtaining a mixture of

$\alpha\beta$- and $\beta\gamma$-isohexenoic acids, along with $\beta$-hydroxyisocaproic acid; the last-named substance is separated by submitting the product to distillation in a current of steam, which carries over the unsaturated acids.

*$\beta$-Hydroxyisocaproic acid*, $CHMe_2\cdot CH(OH)\cdot CH_2\cdot COOH$, is a colourless syrup, which dissolves readily in common solvents; the *silver* salt crystallises from hot water. On heating the acid under ordinary pressure, an oil distils at 203—220°, consisting principally of $\alpha\beta$- and $\beta\gamma$-isohexenoic acids, along with isocaprolactone.

*$\alpha\beta$-Isohexenoic acid*, $CHMe_2\cdot CH\colon CH\cdot COOH$, is isolated by treating the mixture of unsaturated acids with dilute sulphuric acid, which converts the $\beta\gamma$-modification into isocaprolactone (compare Fittig, Abstr., 1895, i, 204); it is a colourless liquid, which boils at 211—212°, and solidifies in solid carbonic anhydride. The *calcium* salt separates from water in white, silky crystals, and the *silver* salt crystallises in needles. Bromine converts the acid into *$\alpha\beta$-dibromisocaproic acid*, which separates from carbon bisulphide in colourless crystals and melts at 127°. Oxidation with potassium permanganate in alkaline solution gives rise to *$\alpha\beta$-dihydroxyisocaproic acid*, which crystallises from a mixture of ether and light petroleum in rosettes of colourless needles, and melts at 108°; the *calcium* salt is anhydrous. *$\beta$-Bromisocaproic acid* is produced when $\alpha\beta$-isohexenoic acid is treated with hydrogen bromide; it is liquid, and, when gently heated with aqueous sodium carbonate, yields isopropylethylene.

*Isobutylidenecyanacetic acid*, $C_7H_9NO_2$, is obtained by heating cyanacetic acid with isobutaldehyde (1 mol.) for eight hours in sealed tubes at 100° (compare Fiquet, Abstr., 1894, i, 32); it crystallises from light petroleum in long needles, and melts at 87—88°. The acid does not combine with bromine, and hot aqueous potash resolves it into isobutaldehyde, ammonia, and malonic acid. The *calcium* and *silver* salts crystallise in white needles, and the *nitrile* boils at 65° under a pressure of 20 mm.; bromine converts the nitrile into the *dibromide*, $C_6H_9NBr_2$, which melts at 30°, whilst hydrolysis with aqueous potash gives rise to ammonia, isocaprolactone, and a mixture of $\alpha\beta$- and $\beta\gamma$-isohexenoic acids. M. O. F.

**Angelica Oil.** By GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1896, **29**, 1811—1816).—The authors have submitted to examination a heavy, brown, oily liquid representing the last runnings obtained by the distillation of angelica roots; this, after being left for some time, deposited a very small quantity of crystals which melted at 74—77°. The separated oil boiled between 125° and 230° under a pressure of 20 mm.; from the viscous residue, light petroleum extracted crystals melting at 68—70°. Both the latter and the crystalline compound deposited from the original oil appear to be anhydrides of a hydroxy-acid. The oil, which had been once fractionated under diminished pressure, was treated with alcoholic potash; the residual oil consisted for the most part of terpenes boiling at 240—270°. From the alkaline solution, on the addition of sulphuric acid, *hydroxypentadecyclic acid*, $C_{15}H_{30}O_3$, separated, which, after crystallisation from ether, melted at 84°; the *barium* salt is a white powder, and the *acetyl* derivative melts at 59°. *Bromopentadecyclic acid*, $C_{15}H_{29}BrO_2$, is obtained by heating the hydroxy-acid with concentrated hydrobromic acid; it melts at 65°. *Iodopentadecyclic acid* melts at 78—79°. Methylethylacetic acid was isolated from the alkaline solution above mentioned after acidification. A. R. L.

**Preparation of Glyceric acid.** By Paul Cazeneuve (*Compt. rend.*, 1896, **122**, 1206—1207).—When silver chloride is heated with excess of sodium hydroxide and glycerol, the latter is converted into glyceric acid without any formation of aldehydes; 144 parts of silver chloride, 46 parts of glycerol, and 80 parts of sodium hydroxide in 500 parts of water are convenient proportions. The silver chloride is first converted into the oxide and afterwards reduced to metallic silver. The glyceric acid is separated from the excess of glycerol by repeated treatments with dry acetone, in which glycerol is insoluble. C. H. B.

**Decomposition of Dihydroxystearic acid into its Optically Active Constituents.** By Paul Freundler (*Bull. Soc. Chim.*, 1895, [3], **13**, 1052—1055).—Two *dihydroxystearic acids*,

$$CH_3\cdot[CH_2]_7\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot COOH,$$

are known, the one obtained from oleïc and the other from elaïdic acid (Gröger, Abstr., 1885, 883, and Saytzeff, Abstr., 1886, 140). These should be racemic modifications, and should be capable of being separated into four optically active dihydroxystearic acids. The author has succeeded in decomposing the acid (m. p. 131°) obtained from oleïc acid into its optically active constituents by means of its strychnine salt. The acid is first converted into its potassium salt, which forms crystalline granules insoluble in water, but soluble in warm alcohol, and a boiling solution of the potassium salt is then mixed with an excess of strychnine sulphate, and warmed for about half an hour; the sulphate of potassium is filtered off, and the filtrate yields first of all crystals of the strychnine salt of the lævo-acid. After concentration, long needles of strychnine sulphate separate out and finally crystalline granules of the strychnine salt of the dextro-acid. The separation is almost complete, and the salts need not be further purified. The acids themselves are readily obtained by decomposing these salts with concentrated hydrochloric acid; both are very sparingly soluble in most solvents at the ordinary temperature. The *ethylic salt* of the lævo-acid crystallises in colourless needles, melts at 98—99°, and has a specific rotatory power $[\alpha]_D = -2{\cdot}1°$. The corresponding *strychnine salt* crystallises with $5H_2O$, and melts at 128—130°. The *ethylic salt* of the dextro-acid resembles that of the lævo-acid, but has a specific rotatory power $[\alpha]_D = +1{\cdot}6°$. These numbers are only approximate, as the solutions used were extremely dilute owing to the slight solubility of the ethylic salt. J. J. S.

**Velocity of Lactone Formation amongst Acids of the Sugar Group.** By Edvard I. Hjelt (*Ber.*, 1896, **29**, 1861—1863).—Attention has already been drawn to a variation in velocity of lactone formation amongst certain sugar acids, and the author has determined the velocity constants for *l*-mannonic, *l*-gulonic, α-glucoheptonic, *l*-arabonic, saccharic, and mucic acids. In the case of gluconic acid, the production of a lactone is so slow, and the regeneration of the hydroxy-acid so rapid, that accurate results could not be obtained by titration. M. O. F.

**Acid Peroxides and their action on reducing Substances.** By LUDWIG VANINO and EDMUND THIELE (*Ber.*, 1896, **29**, 1724—1729).—A number of acid peroxides have been prepared by the method of Pechmann and Vanino (Abstr., 1894, i, 416).—*Succinic peroxide*, $C_4H_4O_4$, is a white, crystalline compound, which is insoluble in all the usual solvents, and explodes violently when heated to 120° in a narrow tube. It also explodes when rubbed or pressed in the dry state. It has strong oxidising properties, and explodes when treated with aniline or strong sulphuric acid. Phenylhydrazine also reacts violently with the peroxide, but in dilute solution converts it into succinimide. Benzoic peroxide, on the other hand, when treated in the same way yields *benzoylphenylhydrazine*, which crystallises in asymmetric tablets melting at 168—170°.

Benzoic peroxide does not liberate sulphur from sodium thiosulphate or decolorise potassium permanganate solution, but otherwise resembles succinic peroxide in its oxidising properties.

*Fumaric peroxide*, $C_4H_2O_4$, is a white, insoluble powder, which detonates faintly at 80°, but otherwise closely resembles the succinic compound.

Acetic peroxide could not be obtained in the solid state. *Phenylacetic peroxide* is soluble in ether, and melts at 41°. It does not appear to be explosive, but decomposes so readily with formation of phenylacetic acid that it could not be obtained pure.

*Orthotoluic peroxide* crystallises from dilute alcohol in indistinct prisms, melting at 60°. It shows all the characteristic properties of the peroxides.

*Camphoric peroxide* appears to be extremely unstable. A. H.

**Action of Ethylic Iodide and Zinc on Ethereal Salts of $\Delta^{\alpha\beta}$-Unsaturated Aliphatic acids.** By ARTHUR MICHAEL (*Ber.*, 1896, **29**, 1791—1792).—Ethylic fumarate, ethylic iodide, and zinc, when digested together for a long time, yield *ethylic ethylsuccinate*, boiling at 230—231°. In the same way, ethylic ethylfumarate, boiling at 122—123° at 15 mm., is obtained from ethylic acetylenedicarboxylate and ethylic iodide; whilst if the portion of the product from ethylic citraconate and ethylic iodide which boils between 235° and 237° is hydrolysed, symmetrical methylethylsuccinic acid (m. p. 174—175°) is obtained. The yield obtained by this method is 20—25 per cent. of the theoretical, whilst the main products of the reaction are compounds of an acid and neutral nature, the investigation of which is not yet complete. A. R. L.

**Synthesis of Camphoronic acid and its Derivatives.** By GUSTAV KOMPPA [and A. BERGROTH] (*Ber.*, 1896, **29**, 1619—1625).—

The results obtained in this investigation on the synthesis of hydroxytrimethylsuccinic acid and its derivatives are in the main the same as those obtained by Auwers and von Campenhausen (this vol., i, 525). A. L.

**Hydrolysis of the Alkyl Substitution Derivatives of Ethylic Malonate.** By EDVARD I. HJELT (*Ber.*, 1896, **29**, 1864—1867; compare this vol., i, 205).—The rates of hydrolysis of ethylic isobutylmalonate and isopropylmalonate have been revised, and the values for ethylic methylmalonate, phenylmalonate, ethylallylmalonate, and propylallylmalonate, determined. The rates of hydrolysis are lower for dialkylic derivatives than for monalkylic, and this property is not correlative with the affinity constant for the acid, but is most probably influenced by steric conditions.

The author discusses his results in the light of Victor Meyer's theory of ethereal salt formation. M. O. F.

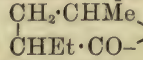
**Alkylated Valerolactones.** By EDVARD I. HJELT (*Ber.*, 1896, **29**, 1855—1859).—In order to study the influence of alkylic groups on the velocity of lactone formation, the author has prepared substituted allylacetic acids, and converted them into the respective lactones; the syntheses were effected by means of ethylic allylmalonate.

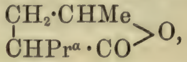
*Ethylallylmalonic acid* is obtained from ethylic allylmalonate, ethylic bromide, and sodium ethoxide, and separates from benzene in large, transparent crystals melting at 107—108°; the *ethylic* salt boils at 233°. Elimination of carbonic anhydride, which occurs at 150°, gives rise to *ethylallylacetic acid*, which boils at 208°.

*Propylallylmalonic acid* crystallises from benzene in microscopic needles, and melts at 115°; the *ethylic* salt boils at 240—241°. Heat converts it into *propylallylacetic acid*, which boils at 221°.

*Isopropylallylmalonic acid* closely resembles the normal derivative, and melts at 112·5°; the *ethylic* salt boils at 232—238°. *Isopropylacetic acid* boils at 217°, and has a rancid odour. The electrical conductivity constants of propyl- and iso-propylallylmalonic acids, $K = 0{\cdot}93$ and $K = 1{\cdot}46$ respectively, approximate to those of other substituted malonic acids (compare Walden, Abstr., 1892, 266).

The lactones were obtained by Fittig's method, treating the unsaturated, monobasic acids with hot, dilute sulphuric acid during 15 minutes, diluting with water, heating again, and finally extracting with ether; the liquid was then agitated with soda, evaporated, and the residue dried by means of potassium carbonate.

*Ethylvalerolactone*,  $\left.\begin{array}{l}CH_2\cdot CHMe\\ |\\ CHEt\cdot CO-\end{array}\right>O$, boils at 216°, and has the characteristic odour of volatile lactones. *Propylvalerolactone*,



$$\left.\begin{array}{l}CH_2\cdot CHMe\\ |\\ CHPr^a\cdot CO\end{array}\right>O,$$

boils at 233°, and *isopropylvalerolactone* at 224°.

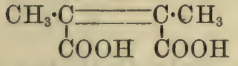
On determining the velocity coefficients of these lactones, the hydroxy-acids were found to arrange themselves in the following order—γ-Hydroxyvaleric acid, *Ac* = 0·0027; isopropyl-γ-hydroxyvaleric acid, *Ac* = 0·0085; propyl-γ-hydroxyvaleric acid, *Ac* = 0·0100; ethyl-γ-hydroxyvaleric acid, *Ac* = 0·0104. M. O. F.

**Intramolecular Change in Unsaturated Acids. The Isomerides of Pyrocinchonic [Dimethylmaleïc] acid.** By RUDOLPH FITTIG (*Ber.*, 1896, **29**, 1842—1843).—Dimethylmaleïc (pyrocinchonic) acid, existing only in the form of the anhydride, has not been hitherto converted into the fumaric modification, and Delisle states that soda has no action on it (Abstr., 1892, 297). This, however, is not the case, and two new acids have been obtained from the anhydride of dimethylmaleïc acid under the influence of 20 per cent. aqueous soda.

*Dimethylfumaric (methylmesaconic) acid*, $C_6H_8O_4$, crystallises in feathery aggregates of long needles, and dissolves sparingly in water; it melts at 240°, and sublimes below this temperature without undergoing decomposition. The *barium* salt crystallises in colourless needles.

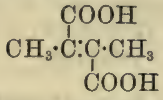
*Methylitaconic acid*, $C_6H_8O_4$, is more readily soluble in water, and crystallises in monosymmetric prisms; it melts at 150—151°, and in part decomposes, undergoing conversion into dimethylmaleïc anhydride and water when distilled. The *barium* salt, which contains $1H_2O$, dissolves with great difficulty in hot water, but is less sparingly soluble in cold water.

The configuration of the three acids is represented by the following formulæ.



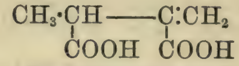
$CH_3\cdot\underset{COOH}{C}=\!=\!=\underset{COOH}{C}\cdot CH_3$

Methylcitraconic acid (dimethylmaleic acid).



$CH_3\cdot\overset{COOH}{C}:\underset{COOH}{C}\cdot CH_3$

Methylmesaconic acid (dimethylfumaric acid).



$CH_3\cdot\underset{COOH}{CH}\text{——}\underset{COOH}{C}:CH_2$

Methylitaconic acid

M. O. F.

**Constitution of Oxalacetic acid.** By ARTHUR MICHAEL and JOHN E. BUCHER (*Ber.*, 1896, **29**, 1792—1793).—Both ethylic oxalacetate and the ethylic derivative of asymmetrical diethoxysuccinic acid are quantitatively converted into oxalacetic acid by cold concentrated hydrochloric acid; the latter, when warmed with acetic chloride or acetic anhydride, yields acetoxymaleïc anhydride (this vol., i, 85). Nef's ethylic ethoxyfumarate (Abstr., 1893, i, 628), when hydrolysed with hydrochloric acid, gives oxalacetic acid, but if hydrolysed with cold, dilute alkali, it gives ethoxyfumaric acid (m. p. 132—134°), which yields the liquid anhydride of ethoxymaleïc acid on treatment with acetic anhydride. Ethoxymaleïc acid likewise yields oxalacetic acid on treatment with hydrochloric acid. Ethylic dibromosuccinate gives ethylic ethoxyfumarate, together with a little ethylic diethoxysuccinate when treated with sodium ethoxide (2 mols.); if more ethoxide is employed, the relative amounts of the two products are reversed. Ethylic acetylenedicarboxylate, when treated with cold sodium hydroxide, gives a mixture of the ethylic derivatives of asymmetrical diethoxysuccinic acid, ethoxyfumaric acid, and ethoxymaleïc acid, whereas, at a higher temperature, only the two latter are formed.

The formation of oxalacetic acid by warming asymmetrical diethoxysuccinic acid, by the action of hydrochloric acid on ethoxyfumaric acid, and that of water on acetoxymaleïc anhydride shows that it contains no carbonyl groups. If that were so, oxalacetic acid would be acetoxymaleïc anhydride, whereas, according to its formation from ethylic ethoxyfumarate, it must be hydroxyfumaric acid; it should also be remarked that the conversion of a fumaroïd modification into a maleïnoïd, by means of hydrochloric acid, has not yet been observed, besides which the stability of oxalacetic acid towards hydrochloric acid is incompatible with the assumption that it is the maleïnoïd modification. The apparent anomaly of these reactions vanishes if it be assumed that the primarily formed hydroxy-acids are labile and change into $COOH·CO·CH_2·COOH$. The ketone constitution must also be assigned to ethylic oxalacetate.

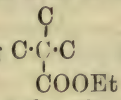
A. R. L.

**Two Stereoisomeric Methylcarbocaprolatonic acids.** By Edvard I. Hjelt (*Ber.*, 1896, **29**, 1860—1861; compare Abstr., 1892, 697).—*Paramethylcarbocaprolactonic acid*, $C_8H_{12}O_4$, is obtained from both para- and μ-methylallylsuccinic acid (*loc. cit.*) by means of Fittig's method for producing lactones; it crystallises from water in well-defined prisms, and melts at 140—141°. The *barium* salt is crystalline.

*μ-Methylcarbocaprolactonic acid* separates on allowing the oily mother liquor of the foregoing acid to deposit crystals; it forms needles melting indefinitely at 60—68°, and dissolves very readily in water. The *barium* salt is crystalline. M. O. F.

**Hydrolysis of Ethereal Salts of certain Tribasic acids.** By Edvard I. Hjelt (*Ber.*, 1896, **29**, 1867—1869; compare this vol., i, 205, and 598).—The rates of hydrolysis of ethylic salts of ethanetricarboxylic, propanetricarboxylic, phenylethanetricarboxylic, ethylethanetricarboxylic, and allylpropanetricarboxylic acids have been determined, and found to diminish in the order indicated. The values for triethylic citrate, aconitate, and camphoronate diminish in the order named.

The author's experiments with dibasic and tribasic acids render it probable that the grouping



$\overset{\displaystyle C}{\underset{\displaystyle COOEt}{C·C·C}}$

is not favourable to hydrolysis; if this indication is trustworthy, the rate of hydrolysis of triethylic camphoronate favours representation of the acid by Bredt's formula rather than Tiemann's. M. O. F.

**Formation of Carbon Chains. XII. Quantitative Study of the Synthesis of Ethereal Salts of Penta-, Hexa-, and Heptabasic Fatty acids.** By Carl A. Bischoff (*Ber.*, 1896, **29**, 1741—1750).—The interaction of methylic sodethanetricarboxylate and methylic bromomalonate proceeds in the normal manner, 51 per cent.

of the product consisting of *methylic propargylpentacarboxylate* (pentandioic-2 : 2 : 3-trimethyloate; propane-1 : 2 : 2 : 3 : 3-pentacarboxylate), which crystallises in four-sided tablets melting at 87—88°. Hydrolysis with hydrochloric acid yields tricarballylic acid. When the corresponding ethylic salt is treated with ethylic chloromalonate, only 7 per cent. of the normal product is formed, along with a little ethylic ethanetetracarboxylate. When the product is washed with water, a portion of the substance becomes hydrolysed, and goes into solution, but the nature of the products formed has not yet been ascertained. The normal product is also formed, to the extent of about 40 per cent., from the ethylic salt and ethylic bromomalonate.

In the case of the ethereal salts of ethanetetracarboxylic acid, no normal product was obtained by the interaction of the ethylic salts and the chloromalonate, about 70 per cent. from the methylic salts and the bromomalonate, and only a very small quantity from the ethylic salts and the bromomalonate, the chief products being ethylic ethanetetradicarboxylate and ethylenetetracarboxylate. This result is quite in accordance with the author's dynamical theory, according to which the nature of the alkyl group should have a special influence on the formation of this ethereal salt. Hydrolysis with hydrochloric acid yields tricarballylic acid.

The formation of the normal product (heptabasic) from ethylic sodiopropane-1 : 2 : 2 : 3 : 3-pentacarboxylate and ethylic bromomalonate could not be definitely proved, since considerable decomposition took place on distillation. No evidence of the formation of butanetetracarboxylic acid, on hydrolysis, could be obtained.

A. H.

**Constitution of Acid Amides.** By ARTHUR LACHMANN (*Amer. Chem. J.*, 1896, **18**, 600—608).—A study of the work which has been done on this question leads the author to the conclusion that the amides fall into two classes—(1) those possessing the ordinary amide formula; such are probably oxamethane, the various carbamides and benzenesulphonamide; and (2) those which have the imido-hydroxy-structure; such are probably acetamide and benzamide. In order to obtain further evidence, the behaviour of amides towards sundry reagents was examined, but without results worthy of discussion, except in the case of phosphorus trichloride. With this reagent, acetamide gives a red, sticky mass containing chlorine, phosphorous acid, ammonia, and acetamide; hydrogen chloride is evolved, but neither acetonitrile nor acetic chloride is formed. Benzamide gives 75 per cent. of bezonitrile. Urethane is destroyed. Oxamethane remains unchanged. This production of benzonitrile from benzamide cannot be a case of mere dehydration, since oxamethane is as sensitive to dehydrating agents as is benzamide, and yet it is not affected by the trichloride. In the author's opinion the benzamide forms an imidochloride as an intermediate product, and must, therefore, contain a hydroxyl group.

A. G. B.

**Action of Nitric acid on Methylamides and Dimethylamides.** By ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1896, **15**, 61—65;

compare Abstr., 1888, 447).—Absolute nitric acid may behave with methylamides and dimethylamides of different acids in one of four different ways.

I. Neither the methylamide nor the dimethylamide is acted on. Examples: Those of nitrobenzoic acid, trichloracetic acid; in the case of the latter, however, the monomethylamide is very slowly acted on, but the dimethylamide not at all. A special case is met with in certain derivatives of oxalic acid; dimethyloxamide readily yields a nitro-derivative, whereas tetramethyloxamide is not acted on.

II. The methylamide yields the corresponding acid, nitric peroxide, and methylic nitrate, whilst the dimethylamide yields the acid and dimethylnitramine. Examples: Trimethylacetic, heptilic, succinic, dimethylmalonic, amidoformic acids, &c.

III. The methylamide yields a stable nitro-derivative, whereas the dimethylamide yields the acid and dimethylnitramine. Examples: Phenylsulphonic, ethylsulphonic, and sulphuric acids.

IV. The methylamide gives a stable nitro-derivative, whilst the dimethylamide undergoes oxidation; one of the methyl groups is removed, and becomes replaced by a nitro-group in such a manner that the dimethylamide yields the same nitro-derivative as the methylamide. Examples: Picric acid, dinitrocresols (ortho- and para-), trinitrometacresol, the methylic and ethylic salts of mono- and di-methylamidoformic acid, which yield in this way nitro-urethanes.

These differences in behaviour must be attributed to the influence of the different negative radicles. J. J. S.

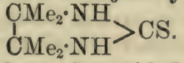
**Action of Nitric acid on Oxalpiperidide.** By Antoine P. N. Franchimont and H. van Erp (*Rec. Trav. Chim.*, 1896, **15**, 66—68). —Oxalpiperidide, for the preparation of which compare Schotten (Abstr., 1882, 983), and Kamensky (*Annalen*, 1882, **214**, 278), readily dissolves in pure nitric acid; very little heat is developed, and the solution is only slightly coloured. No disengagement of gas occurs, and the liquid, when placed in a vacuum for a few days, yields the unaltered piperidide in almost theoretical quantity. Oxalpiperidide thus behaves towards nitric acid like tetramethyloxamide. (Compare previous abstract.) J. J. S.

**Action of Nitric acid on certain Piperidides.** By Antoine P. N. Franchimont and H. J. Taverne (*Rec. Trav. Chim.*, 1896, **15**, 69—75).—The piperidides of oxalic and of alkylcarbonic acids react with nitric acid similarly to the dimethylamides of the corresponding acids. Thus oxalpiperidide is not acted on (see preceding abstract), whereas piperylurethane is oxidised, and at the same time nitrated (*Rec. Trav. Chim.*, 1894, **13**, 334). The authors have prepared three more piperidides, and studied their action towards nitric acid.

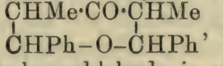
*Trichloracetopiperidide* was obtained by the action of an ethereal solution of trichloracetic chloride on an ethereal solution of piperidine; it forms large, colourless crystals, melts at 45°, and is insoluble in water, and not decomposed when boiled with the same. It dissolves in ether, alcohol, chloroform, benzene, &c., readily forms supersaturated solutions in ether or in light petroleum, and is not acted on by cold nitric acid.

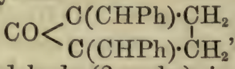
*Benzenesulphonepiperidide* (Hinsberg, Abstr., 1892, 65), and Schotten (Abstr., 1892, 354), when treated with cold nitric acid, is decomposed in much the same way as benzenesulphonedimethylamide (*Rec. Trav. Chim.*, 1883, **3**, 7), and nitropiperidine is one of the products formed.

*Picrylpiperidide* (Turpin, Trans., 1891, **59**, 716, and Schotten, *loc. cit.*), when added to ice-cold nitric acid, is readily acted on, and yields *picrylnitrodehydropiperidide;* this crystallises from alcohol in red needles, melts at 195°, and is hydrolysed when boiled with a 10 per cent. potash solution. J. J. S.

**"Carbothioacetonin."** By Johann Heilpern (*Monatsh.*, 1896, **17**, 229—244).—This name was applied by Städeler (*Annalen*, 1859, **111**, 311, 316) to the compound which Hlasiwetz prepared by the interaction of acetone, carbon bisulphide, and ammonia (*ibid.*, 1850, **76**, 294). The author has prepared the compound, and finds that its molecular formula is $C_7H_{14}N_2S$, and that when oxidised by potassium permanganate, it yields acetonylcarbamide, thus justifying the conclusion that it is *pinacolylthiocarbamide*,  $\begin{array}{l}CMe_2\cdot NH\\ |\\ CMe_2\cdot NH\end{array}\!\!>CS$. The compound crystallises in microscopic, colourless, four-sided, pointed prisms, melts at 240—243° (uncorr.), and dissolves freely in hot alcohol, ether, ethylic acetate, acetone, chloroform, hydrochloric acid, and glacial acetic acid. It is intensely bitter, and chemically indifferent. The *platinochloride* of an *ethyl* derivative $(C_7H_{13}EtN_2S)_2,H_2PtCl_6$, was found to crystallise in small, orange-red tables, and to melt at 161—163° (uncorr.), but the ethyl derivative itself could not be purified, nor could any other well characterised substitution product be isolated.

Acetonylcarbamide *aurochloride* has the anomalous composition $(C_5H_8N_2O_2)_2,HAuCl_4 + 2H_2O$, similar to that found by Heintz for the gold salt of carbamide (*ibid.*, 1880, **202**, 264); it melts at 161—162° (uncorr.). A. G. B.

**Condensation of Ketopentamethylene with Aldehydes.** By Daniel Vorländer and Karl Hobohm (*Ber.*, 1896, **29**, 1836—1841).—The ketone, $C_5H_8O$, isolated from the higher boiling fraction of wood spirit, has been shown by Hentzschel to be adipin ketone (Abstr., 1893, i, 556), and is therefore the cyclic analogue of diethyl ketone. The authors have compared the behaviour of these two substances towards aldehydes, having already shown (this vol., i, 546) that diethyl ketone combines with benzaldehyde (2 mols.), forming the anhydride of a ketoglycol. This substance, which is also produced by the action of benzaldehyde on benzylidenediethyl ketone, has the constitution,  $\begin{array}{l}CHMe\cdot CO\cdot CHMe\\ |\qquad\qquad\quad |\\ CHPh-O-CHPh\end{array}$, and thus the behaviour of diethyl ketone towards benzaldehyde is shown to be quite different from that of acetone; in this respect, however, ketopentamethylene is found to resemble the latter ketone, yielding a dibenzylidene compound, instead of a derivative of pyrone.

*Dibenzylideneketopentamethylene*,  $\mathrm{CO}<\begin{matrix}\mathrm{C(CHPh)\cdot CH_2} \\ \qquad\qquad\quad | \\ \mathrm{C(CHPh)\cdot CH_2}\end{matrix}$, obtained by dissolving adipin ketone and benzaldehyde (2 mols.) in 50 per cent. alcohol, crystallises in yellow needles, melting at 189°; reduction with zinc dust and glacial acetic acid gives rise to a white substance, which probably consists of dibenzylketopentamethylene. The *tetrabromide*, $C_{19}H_{16}Br_4O$, crystallises from glacial acetic acid in needles, and melts, evolving hydrogen bromide, at 175°; when the alcoholic solution is boiled with powdered antimony, dibenzylideneketopentamethylene is regenerated. *Benzylideneketopentamethylene*, $C_{12}H_{12}O$, forms colourless crystals, and melts at 68°.

*Dianisylideneketopentamethylene*, $C_{21}H_{20}O_3$, crystallises from absolute alcohol in lustrous, yellow plates, and melts at 212°. *Dicinnamylideneketopentamethylene* is yellow, and melts at 215—218°.

*Difurfurylideneketopentamethylene*, $C_{15}H_{12}O_3$, is the pyroxanthin of Scanlan, Apjohn, and Gregory, and melts at 163°; the solution in concentrated sulphuric acid is intense violet-blue, the moderately concentrated acid yielding a carmine-red solution. Treatment with excess of bromine in carbon bisulphide solution gives rise to *dibromopyroxanthin tetrabromide*, $C_{15}H_{10}Br_6O_3$, which crystallises from chloroform in colourless needles; when heated at 90—100°, it blackens, but if the temperature is quickly raised to 150°, it becomes grey, melts, and effervesces vigorously. Hot phenol, or boiling alcohol with zinc dust or antimony, converts the tetrabromide into dibromopyroxanthin (Hill, 1876, ii, 456), which melts at 180°.

*Difurfurylideneketohexamethylene* crystallises from alcohol in yellow needles, and melts at 144°; the solution in concentrated sulphuric acid is violet, and in moderately strong acid, carmine-red. *Dibenzylideneketohexamethylene* crystallises in yellow prisms, and melts at 118°.

The application of benzaldehyde in separating the constituents of wood oil and acetone oil is recommended by the authors, who have isolated from the latter a compound which crystallises in needles, and melts at 233°. M. O. F.

**Direct Substitution of Chlorine or Bromine for Nitro-groups by the Aid of Hydrochloric or Hybrobromic acid.** By CORNELIS A. LOBRY DE BRUYN and FREDERIK H. VAN LEENT (*Rec. Trav. Chim.*, 1896, **15**, 84—88).—The authors find that various nitro-compounds (1—2 grams) when heated with saturated aqueous hydrochloric acid (2—3 c.c.) at 200—300° for several hours yield products which contain chlorine in place of the nitro-groups. These chloro-derivatives are best separated from the unaltered nitro-compounds by distillation with steam. Symmetrical trinitrobenzene yields the corresponding trichlorobenzene and a small quantity of tetrachlorobenzene. Orthodinitrobenzene, heated at 250—270° for an hour and a half, yields orthodichlorobenzene. Metadinitrobenzene yields a mixture of metadichloro- and trichloro-benzene. Paradinitrobenzene and parachloronitrobenzene both yield paradichlorobenzene. δ-Tetranitronaphthalene (1 : 2 : 1′ : 4′) yields the corresponding tetrachloronaphthalene, but γ-tetranitronaphthalene yields a pentachloronaphthalene. Symmetrical trinitrobenzoic acid yields symmetrical trichlorobenzene. The nitrophenols are not acted on at 220°, and at higher temperatures are completely decomposed.

Orthodinitrobenzene, when heated with hydrobromic acid at 250—260°, yields orthodibromobenzene. J. J. S.

**Electrolytic Reduction of Nitrobenzene in presence of Hydrochloric acid.** By WALTER LÖB (*Ber.*, 1896, **29**, 1894—1899; compare this vol., i, 533).—When nitrobenzene suspended in hydrochloric acid is placed in a porous cylinder, which is surrounded by dilute sulphuric acid, and a current of 0·6—1 ampère and 5—5·5 volts passed through, an anode of platinum being placed in the sulphuric acid, the nitrobenzene is reduced, with formation of a mixture of ortho- and para-chloraniline. It seems probable that phenylchloramine, $C_6H_5·NHCl$, is formed as an intermediate compound, but direct evidence of this has not yet been obtained. The reduction can also be carried out spontaneously by placing the nitrobenzene and hydrochloric acid in a porous cylinder surrounded by an acid solution of ferrous sulphate, and connecting a carbon rod placed in the cylinder with an amalgamated zinc plate placed in the ferrous sulphate solution. About 20 per cent. of the nitrobenzene appears to undergo some other change, the exact nature of which has not yet been ascertained.

When a solution of nitrobenzene in alcoholic hydrochloric acid is treated in a similar way, the chief product is benzidine, azobenzene and chloraniline being also formed. A. H.

**Orthohalogen Derivatives of Nitrobenzene and of Orthamidophenylic Ethers.** By F. ULLMANN (*Ber.*, 1896, **29**, 1878—1881).—Orthochloronitrobenzene is best prepared by means of Sandmeyer's reaction, "bronze powder," washed with ether, being used instead of precipitated copper; a yield of 65 per cent. is obtained. Orthobromonitrobenzene, which melts at 41·5° and boils at 260° (pressure = 734 mm.), may be prepared in a similar way, nearly 70 per cent. of the theoretical yield being obtained. A quantitative yield of orthoiodonitrobenzene, which boils at 288—289° (pressure = 729 mm.) and melts at 49·5°, is obtained in the same way. *Orthamidophenylic ether* may be readily obtained by the reduction of the corresponding nitro-compound with stannous chloride and hydrochloric acid. It boils at 307—308° (pressure = 728 mm.), and melts at 42·5—43°. The *hydrochloride* melts at 151·5°. A. H.

**Preparation of Orthoisopropylphenol and of Jacobsen's Metapropylphenol.** By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1895, [3], **13**, 981—984).—The author contradicts Claus and Schulte's statement (Abstr., 1887, 264) that when cumene is treated with sulphuric acid for four days on the water bath, it yields more ortho- than para-sulphonic acid; he states that 100 grams of cumene treated according to Claus and Schulte's method never yields more than 25 grams of the barium salt of the ortho-acid. *Orthoisopropylphenol* was prepared by fusing the potassium salt of the cumene-orthosulphonic acid with three times its weight of potash. The indophenol derivative could not be obtained in a crystalline form.

The author gives minute details for the preparation of Jacobsen's metapropylphenol (Abstr., 1878, 731), as considerable care has to be taken.

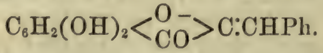
The indophenol of Jacobsen's compound has been prepared by the general method previously described (Abstr., 1895, i, 416); it melts at 73—74°. J. J. S.

**Isopropylbenzoquinone. Constitution of Jacobsen's Metapropylphenol.** By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1895, [3], **13**, 984—985).—*Isopropylbenzoquinone* crystallises in yellow prisms, melts at 28·4°, but when once fused does not readily solidify. It is very volatile, and is readily decomposed both by heat and light; it is sparingly soluble in cold water, but readily in alcohol, ether, and benzene. The quinone is readily reduced by sodium hydrogen sulphite solution saturated with sulphurous acid, and yields *isopropylquinol*, which crystallises in long, hard, transparent needles, and melts at 130—131°.

The indophenol derivative of Jacobsen's metapropylphenol has yielded the above quinone under the usual treatment (Abstr., 1895, i, 416), it therefore follows that Jacobsen's metapropylphenol is really metaisopropylphenol. J. J. S.

**Paracymoquinone.** By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1895, [3], **13**, 979—980).—This quinone, which is isomeric with thymoquinone, is best obtained by treating the indophenol derived from $\alpha$-hydroxyparacymene according to the general method (Abstr., 1895, i, 416). It is a yellowish-red liquid heavier than water, and does not solidify at $-15°$, but when suddenly cooled by means of a jet of methylic chloride, it solidifies to bright golden needles, which melt at 18°. It is readily acted on by light, is rapidly changed when exposed to the air, and is decomposed on heating. It is only very sparingly soluble in water, but readily in alcohol and ether. It is readily reduced to the corresponding *quinol* by means of a solution of sodium hydrogen sulphite saturated with sulphurous acid; the quinol crystallises in brilliant plates, melts at 138°, and is readily oxidised back to the quinone. J. J. S.

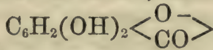
**Action of Benzaldehyde on Chloracetopyrogallol.** By LUDWIG KESSELKAUL and STANISLAUS VON KOSTANECKI (*Ber.*, 1896, **29**, 1886—1891).—The authors consider that the substance described as dihydroxyflavone (Friedländer and Rüdt, this vol., i, 439) which is formed by the action of benzaldehyde on chloracetopyrogallol, or anhydroglycogallol, is in reality *benzylideneanhydroglycogallol*,



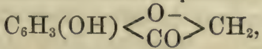
$$C_6H_2(OH)_2<\begin{matrix}O\,-\\CO\end{matrix}>C{:}CHPh.$$

The compound does not agree with the flavone derivatives in many of its properties, thus it yields an orange-red and not a yellow solution in sulphuric acid, it dyes orange and not yellow on an alumina mordant, and it yields a yellow and not a colourless *diethyl ether;* the latter melts at 115°, and forms long, yellow needles. The compound is, moreover, formed by the direct action of benzaldehyde on anhydroglycogallol in presence of dilute potash.

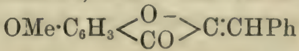
Resacetophenone and its monethyl ether do not condense with benzaldehyde in presence of dilute aqueous soda, whereas the diethyl ether, under these circumstances, yields 2 : 4-*diethoxybenzylideneacetophenone*, $C_6H_3(OEt)_2{\cdot}CO{\cdot}CH{:}CHPh$, which forms long, pointed crystals, and melts at 92—93°. A. H.

**Flavone Derivatives. II.** By PAUL FRIEDLÄNDER and HERMANN RÜDT (*Ber.*, 1896, **29**, 1751—1756; compare this vol., i, 439).—*Anhydroglycopyrogallol*,  $C_6H_2(OH)_2<\substack{O-\\ CO}>CH_2$, like indoxyl, reacts with benzaldehyde to form the dihydroxyflavone already described. With isatin, it reacts to form an analogous derivative, $C_{16}H_9NO_5$, which crystallises in flat, reddish-brown needles, and dyes wool mordanted with chromium a brownish-violet. The *triacetyl* derivative crystallises in yellowish-red needles, and melts at 227°.

These compounds closely resemble chrysin in properties, and hence probably have the constitution assigned, and are not simple condensation products. This constitution is also rendered probable by the analogy of the derivatives of bromoresacetophenone and bromopeonol.

*Diacetylresacetophenone* crystallises in colourless needles, melting at 38°, and, when treated with bromine in acetic acid solution, yields *monobromodiacetylresacetophenone*, $C_6H_3(OAc)_2{\cdot}CO{\cdot}CH_2Br$. When this compound is boiled with aqueous soda, it yields a compound of the formula  $C_6H_3(OH)<\substack{O-\\ CO}>CH_2$, which crystallises in white, sparingly soluble needles, and melts and decomposes at 243°. This substance reacts with aldehydes in a similar manner to anhydroglycopyrogallol. Condensation products have been obtained with benzaldehyde, furfuraldehyde, and a number of other substances.

Bromoresacetophenone, $C_6H_3(OH)_2{\cdot}CO{\cdot}CH_2Br$, loses hydrogen bromide and passes into an anhydride, which yields the same condensation products with aldehydes as the original bromo-compound.

Bromopeonol, $OMe{\cdot}C_6H_3(OH){\cdot}CO{\cdot}CH_2Br$ [$OMe : OH : CO{\cdot}CH_2Br = 4 : 2 : 1$], cannot be converted into an anhydride, but yields condensation products with aldehydes, which are quite analogous to those already described. This is a strong argument in favour of the flavone constitution of these derivatives, since the formation of a substance of the constitution  $OMe{\cdot}C_6H_3<\substack{O-\\ CO}>C{:}CHPh$ would seem to require the intermediate formation of an anhydro-compound.

*Monobromacetylpeonol*, $OMe{\cdot}C_6H_3(OAc)CO{\cdot}CH_2Br$, melts at 86—87°. Its condensation products with aldehydes are yellowish. The *piperonaldehyde derivative* melts at 175°. A. H.

**New Apiole.** By GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1896, **29**, 1799—1811).—The highest boiling fraction of a sample of dill oil, representing about 30 per cent. of the total oil, was submitted to fractional distillation under a pressure of 11 mm. About two-thirds passed over at 162°, and consisted of a new *apiole;* this differs from ordinary apiole from parsley in the position of the methylene relative to the methoxy-groups. It is an oily liquid, which could not be solidified by cooling, and boils at 285° under the ordinary pressure, decomposing slightly; it is almost insoluble in water, but dissolves in other ordinary solvents. Aqueous alkalis do not attack it, and it exhibits the same behaviour towards concentrated sulphuric acid as ordinary apiole. The *monobromodibromide*, $C_{12}H_{13}Br_3O_4$, crystallises in white needles, and melts at 110°.

When the new apiole is heated at 150—170° with sodium ethoxide for 6—10 hours an isomeric *isoapiole* is formed by reason of the transformation of the allyl group into the propenyl group; a phenolic compound is formed as a bye-product. The isoapiole crystallises from light petroleum in colourless, monoclinic prisms,

$$a:b:c = 0{\cdot}86863:1:0{\cdot}46102;\ \beta = 79°\ 30',$$

melts at 44°, and boils at 296° with slight decomposition; it gives a red coloration with concentrated sulphuric acid. The *monobromobromide* melts at 115°. The bye-product, which is probably identical with the compound obtained in a similar manner from ordinary isoapiole (Bartolotti, Abstr., 1892, 1315), boils at 189—191° under a pressure of 16 mm. The composition which Bartolotti has assigned to his substance is, in the author's opinion, inaccurate; thus, when apionol is methylated and subsequently oxidised with dilute permanganate, it yields *trimethylapionolic acid*, $OH{\cdot}C_6H(OMe)_3{\cdot}COOH$, which melts at 139—140°. It appears to have the same constitution as the phenol obtained from isosafrole (Abstr., 1892, 972).

On oxidation with permanganate, isoapiole from dill oil behaves similarly to isoapiole from parsley, and yields apiolic acid, apiolaldehyde, and apioleketonic acid. Whereas apioleketonic acid yields, on fusion with potash, apion (m. p. 79°), the corresponding acid from dill oil yields a liquid product on similar treatment.

*Apiolaldehyde* forms long, white needles, and melts at 75°. *Apiolic acid* crystallises in long, slender, white needles, melts at 151—152°, and is readily soluble in the ordinary solvents except water. *Apiolketonic acid* forms pale yellow plates, and melts at 175°.

The apioles from both sources are derived from the same apionol, $C_6H_2(OH)_4$. When the apiole from dill oil is fused with potash, it yields a *dimethylapionolcarboxylic acid*, a syrup which decomposes at 283° into carbonic anhydride and *dimethylapionol*, $C_6H_2(OH)_2(OMe)_2$, the *acetyl* derivative of which melts at 85°. Tetramethylapionol, $C_6H_2(OMe)_4$, melts at 89°, and not at 81° as previously stated (Abstr., 1890, 36).

When the apiolic acid from dill oil is brominated, *dibromapione*, $C_9H_8Br_2O_4$, is obtained; it melts at 92°, and yields the corresponding *apion* on treatment with sodium ethoxide. A. R. L.

**Mercury Salts of Anilides.** By HENRY L. WHEELER and B. W. McFARLAND (*Amer. Chem. J.*, 1896, **18**, 540—547).—*Mercury formanilide*, Hg(NPh·CHO)$_2$, is best prepared by dissolving formanilide and mercuric bromide in alcohol, adding the calculated quantity of sodium ethoxide, and diluting with water; it crystallises from water in colourless needles, and melts at about 194°. When it is suspended in benzene, and benzoic chloride (1 mol.) is added, it is converted into *chloromercury formanilide*, CHO·NPh·HgCl, which crystallises from water in lustrous, colourless plates, and melts at 191°. On concentrating the benzene solution, formylbenzanilide crystallises out, identical with the compound obtained from silver formanilide and benzoic chloride (this vol., i, 478). *Bromomercury formanilide* was prepared by suspending mercury formanilide in carbon bisulphide, and adding bromine (1 mol.) to the cooled liquid. *Iodomercury formanilide* was prepared in like manner. *Mercury formanilide acetate*, CHO·NPh·Hg·OAc, crystallises in colourless, slender prisms when mercury acetate is mixed with formanilide in alcohol and the solution evaporated.

*Mercury formoparatoluidide* is prepared like the anilide; it crystallises from water in colourless needles; when treated with benzoic chloride, it yields *chloromercury formoparatoluidide*, which crystallises in colourless needles, and *formylbenzoparatoluidide*, which crystallises in colourless prisms, and melts at 101°.

*Acetylbenzanilide* is prepared in the same way as formylbenzanilide; it crystallises in long needles, and melts at 68°. *Mercury* sym-*tribromacetanilide*, $(C_6H_2Br_3NAc)_2Hg$, crystallises from 50 per cent. alcohol in aggregates of needles. *Mercury formyl-α-naphthylamine*, $Hg[N(C_{10}H_7)\cdot CHO]_2$, crystallises in colourless needles.

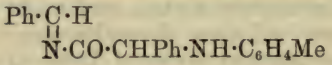
The authors are of the opinion that the reaction of these mercury salts with benzoic chloride, resulting in the formation of a bi-acid anilide, is sufficient evidence to show that the mercury is united with the nitrogen of the anilide. A. G. B.

**New Reactions and New Isomerides of Anil Compounds.** By WILHELM VON MILLER and JOSEF PLÖCHL (*Ber.*, 1896, **29**, 1729—1741).—When benzylideneparatoluidine is heated in alcoholic solution with potassium cyanide, an acid of the formula

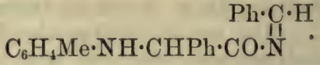
$$CHPh\!:\!N\cdot C(OH)(COOH)\cdot CHPh\cdot NH\cdot C_6H_4Me,$$

and two isomeric substances of the formula $C_{22}H_{20}N_2O$, are formed. The same two isomeric compounds are also obtained by the action of potassium cyanide on an alcoholic solution of benzylidenetoluidine and benzaldehyde, paratolilbenzoïn being also formed, and by the action of benzaldehyde on phenyltoluido-acetonitrile. One of these compounds crystallises in vitreous, monoclinic prisms, and melts at 197°. It is readily soluble in alcoholic potash, and combines with bromine to form an unstable compound. The isomeride crystallises in very small needles, melts at 261°, and is sparingly soluble in solvents of low boiling point. It is soluble with difficulty in alcoholic potash.

Each of these substances is converted by hot alcoholic potash into a mixture of the two isomerides, whilst the substance melting at 197° is converted into the isomeride by heating above its melting point or by heating with alcoholic potassium cyanide. Both the compounds are hydrolysed by hydrochloric acid, with formation of benzaldehyde, ammonia, and phenyltoluidoacetic acid, which melts at 178—182°, and not at 167—170° as stated by Stoeckenius (*Jahresber.*, 1878, 779). The two compounds are, therefore, probably stereoisomeric, and have the following formulæ.



$$\begin{array}{l} Ph\cdot C\cdot H \\ \quad\ \, \| \\ \quad\ \, N\cdot CO\cdot CHPh\cdot NH\cdot C_6H_4Me \end{array}$$



$$\begin{array}{r} Ph\cdot C\cdot H \\ \| \ \ \\ C_6H_4Me\cdot NH\cdot CHPh\cdot CO\cdot N \end{array}.$$

The acid product is also formed in small quantity by the action of potassium cyanide on benzaldehyde and benzylidenetoluidine. It crystallises in small, soft prisms, and melts at 213° with evolution of carbonic anhydride. When heated with hydrochloric acid, it yields the same products as the two isomerides mentioned above. The *anhydride* forms silky needles, and melts at 215°. The *nitrile* is formed by the action of potassium cyanide on a mixture of phenyltoluidoacetonitrile and benzaldehyde. It is a white, granular powder, and melts and decomposes at 262°. A. H.

**Behaviour of certain Diazo-compounds towards Potassium Sulphite.** By EUGEN BAMBERGER and EMIL KRAUS (*Ber.*, 1896, **29**, 1829—1835; compare von Pechmann, Abstr., 1895, i, 370).—The solution of potassium sulphite employed in the authors' experiments was prepared by saturating with sulphurous anhydride a solution of caustic potash in 5 parts of water, and treating the liquid with potassium carbonate until strongly alkaline.

Paranitrodiazobenzene methyl ether, when agitated in ethereal solution with the potassium sulphite solution diluted with 10 parts of water, yields the *dipotassium* salt of paranitrophenylhydrazinedisulphonic acid, $NO_2\cdot C_6H_4\cdot N(SO_3K)\cdot NH\cdot SO_3K$, which separates in small, sulphur-yellow needles, and dissolves readily in hot water.

*Paranitrophenylhydrazine*, $NO_2\cdot C_6H_4\cdot NH\cdot NH_2$, is obtained in theoretical quantity on heating the foregoing salt with 18 per cent. hydrochloric acid on the water bath; it melts at 157°, and the *hydrochloride* crystallises in lustrous, brownish-red leaflets.

The action of potassium sulphite on potassium paranitroisodiazobenzene gives rise to the dipotassium and *tripotassium* salts of paranitrophenylhydrazinedisulphonic acid, which crystallises in flat, lustrous, ruby needles, and yields the dipotassium salt under the influence of carbonic anhydride; along with these substances, potassium paranitrophenyldiazosulphonate is produced. Paranitrodiazobenzene nitrate also yields the dipotassium salt, or potassium paranitrophenyldiazosulphonate, according to the conditions of the experiment; if an aqueous solution of the latter is rapidly cooled and vigorously agitated, lustrous, golden-yellow leaflets separate, consisting of an *isomeride*, which, when suspended in water, assumes the original form in the course of a day or two. The yellow modification is also produced when an aqueous solution of paranitrodiazobenzene nitrate at −2° is treated with the sulphite solution, but the substance, even when washed with ice-cold water and preserved at low temperatures, becomes superficially brown, and acquires the odour of nitrobenzene and sulphurous anhydride; the dry product resinifies or explodes spontaneously. The labile modification is more readily soluble in water than the isomeric form, from which it differs, also, in the property of instantaneously developing colour with alkaline solutions of phenols; the aqueous solution decolorises potassium permanganate and iodine solutions.

The action of potassium sulphite on the potassium derivatives of normal and isodiazobenzene gives rise to potassium benzenediazosulphonate. M. O. F.

**Aldehydates of Phenylhydrazine.** By Henri E. Causse (*Compt. rend.*, 1896, **122**, 1274—1277).—Phenylhydrazine hydrogen tartrate is prepared in a crystalline form by dissolving 100 grams of tartaric acid in 500 c.c. of alcohol, adding 50 grams of phenylhydrazine and allowing the mixture to remain for 24 hours in a cool place. After separation and drying by pressure the crystals are washed with ether.

*Acetaldehyde diphenylhydrazine*, $CMeHO,2N_2H_3Ph$, is prepared by adding a solution of 10 grams of aldehyde in 90 grams of water to a solution of 50 grams of the hydrogen tartrate in 250 c.c. of water. It forms white, brilliant crystals which melt at 77·5°, and decompose and become yellow in contact with air. It also decomposes slowly in closed vessels. When distilled with dilute sulphuric acid, it yields aldehyde, and with barium hydroxide it yields phenylhydrazine.

*Benzaldehyde diphenylhydrazine*, $C_6H_5{\cdot}CHO,2N_2H_3Ph$, is obtained in a similar way, and crystallises from boiling alcohol in long, white needles which melt at 154° and becomes slightly yellow when exposed to air. When distilled with dilute sulphuric acid, it yields benzaldehyde and benzoic acid, and with barium hydroxide it yields phenylhydrazine. C. H. B.

**Constitution of Derivatives of Formic acid.** By Paul C. Freer and P. L. Sherman, jun. (*Amer. Chem. J.*, 1896, **18**, 562—584).—Formylphenylhydrazide was prepared by mixing 200 grams of phenylhydrazine with 200 grams of concentrated formic acid, and cooling the mixture. By dissolving it (59 grams) in a solution of sodium (10 grams) in absolute alcohol and pouring the solution into ether, *sodioformylphenylhydrazide*, $N_2HPhNa{\cdot}CHO$, is obtained in aggregates of felted needles after a short time. This compound decomposes rapidly in the air, aniline, phenylhydrazine, and sodium hydrogen carbonate being the chief products.

Ethylic iodide and formylphenylhydrazide do not react in a sealed tube at 100°; but when ethylic iodide and sodium formylphenylhydrazine are mixed in alcoholic solution, the alcohol and excess of ethylic iodide subsequently distilled off, and the residue poured into water, a heavy, colourless oil separates and solidifies on standing. This compound is *formylphenyl-α-ethylhydrazide*, $NEtPh{\cdot}NH{\cdot}CHO$, for, when reduced by sodium in amylic alcohol, it yields unsymmetrical phenylethylhydrazine, ethylaniline, and ammonia; it forms needle-shaped crystals, melts at 78—79°, and dissolves easily in all organic solvents—except light petroleum; attempts to further ethylate it by means of ethylic iodide failed, but when it is heated under pressure at 100° with sodium ethoxide and ethylic iodide, *formylphenyldiethylhydrazide* is formed. This is a pale yellow, light oil, boiling at 139—140° (5 mm. pressure); by reduction in the manner referred to above, it yields ethylamine and ethylaniline; alcoholic potash does not remove an ethyl group from it; neither phenylhydrazine nor sodium reacts with it.

When dry sodioformylphenylhydrazide is suspended in dry ether, and heated with ethylic iodide in a stoppered bottle at 100°, *formylphenyl-β-ethylhydrazide*, NHPh·NEt·CHO, is formed, which may be isolated by washing the ethereal solution with water, and drying and distilling it; the residual β-compound crystallises from alcohol in large rhombohedra, melts at 106°, and dissolves in all ordinary solvents, save light petroleum and water; much α-compound may be present in it if the sodium salt be not free from alcohol. The possible view that the compound is an imido-ether is negatived by its stability towards alkalis, and by the fact that it yields aniline and ethylamine by reduction such as has been described. The β-ethyl-derivative does not react with ethylic iodide and sodium ethoxide.

No evidence of the existence of a hydroxyl group in formylphenylhydrazide could be obtained by attacking the compound with acetic anhydride. The action of benzoic chloride and sodium ethoxide on formylphenylhydrazide leads to the formation of mono- and dibenzoylphenylhydrazide; the *sodium* derivative of the latter was prepared.

The behaviour of formanilide towards ethylic chlorocarbonate is shown to conform with that of silver formanilide to the same ethereal salt (compare Wheeler and Boltwood, this vol., i, 478). *Sodium formamide* and *silver formamide* are described. The action of sodium on ethylic formate yielded sodium ethoxide, carbonic oxide, and hydrogen as final products, but sodium ethylic formate appeared to exist as an intermediate compound, and a similar transitional existence of sodium amylic formate was clearly indicated when amylic formate was substituted for the ethylic salt.

The authors claim that the foregoing experimental work shows that in sodioformylphenylhydrazide the sodium is attached to nitrogen, and that, therefore, no hydroxyl group is present. There is no evidence of the presence of an aldehyde group, the existence of which in formic acid has been claimed by some, mainly because of the ease with which the acid is oxidised. In the salts of formanilide there is evidence of a hydroxyl grouping (compare Comstock and Kleeberg, Abstr., 1890, 1414), but the authors hesitate to say the same of formanilide itself. A. G. B.

**Phenylhydrazones and Oxime of Protocatechuic Aldehyde.** By RUDOLF WEGSCHEIDER (*Monatsh.*, 1896, **17**, 245—252).—This paper contains the details of the preparation of the above compounds, which have already been described (Abstr., 1894, i, 79). The phenylhydrazone of higher melting point is designated the α-derivative, that of lower melting point being the β-form. Several cases of isomerism among the aldehydephenylhydrazones are now known (compare this vol., i, 361). The oxime melts and decomposes at 149—151°. A. G. B.

**Action of Hydroxylamine on Nitrobenzene.** By ANGELO ANGELI (*Ber.*, 1896, **29**, 1884—1885).—Hydroxylamine reacts with nitrobenzene in alcoholic solution in presence of sodium ethoxide with formation of phenylnitrosohydroxylamine, NO·NPh·OH.

A. H.

**Use of Antimony Trichloride in the Synthesis of Aromatic Ketones.** By WILLIAM J. COMSTOCK (*Amer. Chem. J.*, 1896, **18**, 547—552).—Antimony trichloride may be substituted for aluminium trichloride for the purpose of condensing any acid chloride of moderately high boiling point with an aromatic hydrocarbon. The mixture is heated in a reflux apparatus by means of a paraffin bath, the temperature being gradually raised to 200°. When no more gas is evolved, the mass is washed with strong hydrochloric acid in a separator to remove antimony; the ketone may then be dissolved in ether, and the solution dried by potassium carbonate and distilled. As an example of the method, the following recipe for the production of benzophenone is given:—Benzoic chloride 112 grams, benzene 70 grams, antimony trichloride 300 grams; with these proportions, the action is complete in about 12 hours. The application of the process to the formation of the tolyl phenyl ketones, and of paraxylyl ketone is also given. The yields are from 70 to 80 per cent. of the theoretical proportion. A. G. B.

**Halogen Substitution Products of Resacetophenone [2 : 4 : 1-Dihydroxyacetophenone] and of its Diethylic Ether.** By R. SEGALLE (*Monatsh.*, 1896, **17**, 314—326).—*Dichlorodihydroxyacetophenone* separates when chlorine is passed into an acetic acid solution of dihydroxyacetophenone; it forms white crystals, melts at 195—196°, and dissolves in ether, alcohol, glacial acetic acid, and benzene, but not in water. Bromodihydroxyacetophenone has not yet been prepared. *Diethylic dibromodihydroxyacetophenone ether* was prepared both by ethylating dibromodihydroxyacetophenone (Abstr., 1894, i, 521) and by brominating diethylic dihydroxyacetophenone ether in carbon bisulphide; the product, however, is not the same. The *α-ether*, prepared by the first method, is white, melts at 51—52°, and dissolves in benzene, strong acetic acid and alcohol, but not in water. The *β-ether* crystallises in white needles, and melts at 127—129°. When bromination of diethylic dihydroxyacetophenone ether is conducted in acetic acid solution, *diethylic tribromodihydroxyacetophenone ether* is the chief product; it forms yellowish-white crystals, melts at 132—133°, and dissolves in alcohol and glacial acetic acid. *Tribromodihydroxyacetophenone*, prepared by brominating dihydroxyacetophenone in glacial acetic acid with excess of bromine, forms yellow crystals and melts at 112—113°. *Iododihydroxyacetophenone* crystallises in yellowish-white laminæ, and melts at 158—159°.

A. G. B.

**Ethers of Unsaturated Hydroxy-ketones.** By STANISLAUS VON KOSTANECKI and M. SCHNEIDER (*Ber.*, 1896, **29**, 1891—1894).—3-*Ethoxybenzylideneacetophenone*, $OEt\cdot C_6H_4CH\colon CH\cdot COPh$, crystallises from alcohol in yellowish prisms which melt at 75°, and form an orange-yellow solution in sulphuric acid.

4-*Ethoxybenzylideneacetophenone* forms yellowish, quadratic tablets melting at 63°, and also gives an orange-yellow solution in sulphuric acid.

*Piperonalacetophenone*, $CH_2O_2\colon C_6H_3\cdot CH\colon CH\cdot COPh$, is formed by the condensation of piperonaldehyde with acetophenone, and crystallises in long, yellow needles melting at 122°.

5-*Bromo*-2-*hydroxybenzylideneacetophenone*,

$$OH\cdot C_6H_3Br\cdot CH\colon CH\cdot COMe,$$

crystallises in yellowish prisms melting at 154—155°. It forms an orange coloured solution in sulphuric acid.

5-*Bromo*-2-*acetoxybenzylideneacetone* forms colourless prisms melting at 89—90°.

5-*Bromo*-2-*benzoxybenzylideneacetone*, $OBz\cdot C_6H_3Br\cdot CH\colon CH\cdot COMe$, crystallises in prismatic needles melting at 123°.

5-*Bromo*-2-*ethoxybenzylideneacetone* crystallises in needles melting at 106—107°.

*Di*-2-*ethoxybenzylidenetriacetophenone*,

$$COPh\cdot CH[CH(CH_2\cdot COPh)\cdot C_6H_4\cdot OEt]_2,$$

is obtained from 2-ethoxybenzaldehyde and acetophenone. It crystallises in needles, and melts at 190—192°.

The corresponding *meta-compound* melts at 225°, and the *para-compound* at 226—227°.

*Dipiperonaltriacetophenone* melts at 253—257°. A. H.

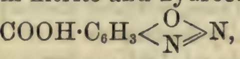
**Action of Methyl alcoholic Potash on 2 : 4 : 6-Trinitrobenzoic acid.** By FREDERIK H. VAN LEENT (*Rec. Trav. Chim.*, 1896, **15**, 89—91; compare this vol., i, 147).—When a solution of trinitrobenzoic acid in methylic alcohol is treated with just sufficient caustic potash for neutralisation, a white precipitate of the potassium salt of the acid separates, if the solution is sufficiently concentrated. With an excess of alkali, a deep red precipitate is formed, but this varies in composition, and probably contains a considerable quantity of the colourless potassium salt. The red compound may be obtained in a pure form by adding to a boiling dilute solution of the acid in methylic alcohol (1·5 gram in 200 c.c.) the requisite quantity of alkali (2 mols. to 1 of acid). On cooling, brown-red crystals, having a strong metallic lustre, are deposited. These have the composition

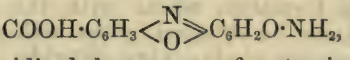
$$C_6H_2(NO_2)_3\cdot COOK,2MeOK,MeOH.$$

A good yield of the same compound is obtained when the requisite quantity of potassium methoxide is added to a concentrated solution of the acid in absolute methylic alcohol. The crystals have a bitter taste, and explode when heated.

The authors state that the red solution obtained on adding an excess of caustic potash solution to trinitrobenzoic acid contains potassium nitrite (compare V. Meyer, this vol., i, 419). After a lapse of several days, the above solution was acidified with hydrochloric acid, and extracted with ether; a reddish-brown oil was thus obtained, soluble in water, alcohol, and ether, but it could not be made to crystallise; it contains a strong *acid*, which gives rise to red *salts*. On boiling with barium carbonate, carbonic anhydride is evolved, and a gelatinous *barium* salt is formed. J. J. S.

**3 : 4-Nitrohydroxybenzoic acid.** By Emil Diepolder (*Ber.*, 1896, **29**, 1756—1760).—3 : 4-Nitrohydroxybenzoic acid can be prepared by Barth's method, by the action of dilute nitric acid (1 : 6) on parahydroxybenzoic acid, and may be purified by means of the barium salt. 2 : 4-Dinitrophenol is formed in small quantity, together with the acid, particularly if the temperature is allowed to rise. The *ammonium* salt crystallises with water in long, bronze needles, melting and subliming at about 220°; the sublimate consists of small, yellow, rhombic crystals. Deninger's method for the preparation of the acid by the action of dilute sulphuric acid on a mixture of sodium nitrite and parahydroxybenzoic acid is inferior to Barth's dinitrophenol, being always formed in considerable quantity. 3 : 4-Amidohydroxybenzoic acid, formed by reduction of the nitro-acid by means of tin and hydrochloric acid, has been previously described; the *acetate* crystallises in flat rhombohedra, and when distilled, yields orthamidophenol.

When acted on by sodium nitrite and hydrochloric acid, the amido-acid yields a *diazoxide*,  $\mathrm{COOH{\cdot}C_6H_3}<^{\mathrm{O}}_{\mathrm{N}}>\mathrm{N}$, which crystallises in yellow needles, darkens at about 110°, and explodes at 116—121°, according to the rapidity with which it is heated; it immediately becomes red when exposed to sunlight, dissolves in soda with a green and in sodium carbonate with a reddish-yellow coloration; dilute sulphuric acid added to the solutions gives rise to black and red flocculent precipitates respectively.

*Amidophenoxazonecarboxylic acid*,  $\mathrm{COOH{\cdot}C_6H_3}<^{\mathrm{N}}_{\mathrm{O}}>\mathrm{C_6H_2O{\cdot}NH_2}$, is formed when the amido-acid is oxidised by means of potassium dichromate and dilute sulphuric acid; it is sparingly soluble and crystallises from ethylic benzoate in needles. The *ammonium* salt is pale red and flocculent, and its aqueous solution, when acidified with acetic acid, gives a dark red, flocculent precipitate, which is soluble in dilute sulphuric acid, showing that the oxazone is both an acid and a feeble base. The *calcium* salt crystallises with $5H_2O$ in small, dark red needles; the *barium* salt forms pale red, microscopic needles; the silver salt could not be prepared, as metallic silver is immediately deposited. The constitution of the oxazone is deduced from its analogy to the compound prepared by O. Fischer and O. Jonas by the oxidation of orthamidophenol; the absence of an imide or hydroxyl group is shown by the composition of the salts, and the monobasicity by titration. J. B. T.

**Attempts to prepare Optically Active Parahydroxymetamethylbenzoic acids.** By LEOPOLD RÜGHEIMER (*Ber.*, 1896, **29**, 1967—1969; compare V. Meyer and Heyl, this vol., i, 146).—The author describes experiments which indicate that, by means of the cinchonine salt, a modification of parahydroxymetamethylbenzoic acid may be obtained, the ammonium salt of which is lævorotatory.

M. O. F.

**Constitution of Ethyl-β-resorcylic acid.** By GEORG GREGOR (*Monatsh.*, 1896, **17**, 225—228; compare this vol., i, 171).—*Ethylic* ethoxy-β-resorcylate is obtained by heating an alcoholic solution of the potassium salt with ethylic iodide on the water bath; it crystallises from alcohol in long, colourless needles, and melts at 45°. It does not develope a coloration with ferric chloride, and is readily hydrolysed by potash.

M. O. F.

**Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Hydrocarbons of the Benzene Series in Presence of Aluminium Chloride.** By LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 1207—1209; compare this vol., i, 551). Toluene and ethylic chloroglyoxylate yield *ethylic paracresylglyoxylate*, which is readily converted into *paracresylgyloxylic acid*. The latter, contrary to the statement of Roser, is a very stable substance, forms beautiful crystals which melt at 97°, and boils without decomposing at 164° under a pressure of 10 mm. When distilled under ordinary pressure, it splits up into a mixture of aldehyde and paratoluic acid.

Metaxylene yields *ethylic metaxylylglyoxylate*, which boils at 165° under a pressure of 10 mm. without decomposing, and forms crystals which melt and partially decompose at 56°. The corresponding acid melts at 60°, and boils at 170° under a pressure of 10 mm.; it is readily converted into metaxylylcarboxylic acid melting at 125°.

Cymene (paraisopropyltoluene) yields *ethylic cymylglyoxylate*, which melts at 180°. Ethylcymene is formed at the same time, probably because ethylic chloride is produced by the action of the hydrogen chloride on the ethyloxalic chloride, and at the moment of its formation reacts with the cymene. Ethylcymene, however, cannot be obtained by the action of ethylic bromide on cymene in presence of aluminium chloride. *Cymylglyoxylic acid*, when distilled under ordinary pressure, yields aldehyde, a *cymenecarboxylic acid*, and a pale yellow oil, which boils at 220° under a pressure of 10 mm., and has the composition of cymophenone, $C_{10}H_{13}\cdot CO\cdot C_{10}H_{13}$. The latter is most probably produced by the action of heat on the cymylcarboxylic acid.

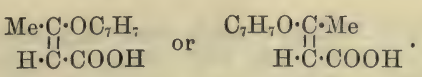
Anisoïl yields *ethylic anisoylcarboxylate*, a pale yellow, oily liquid which boils at 183° under a pressure of 10 mm.

Anisoylcarboxylic acid, which has previously been obtained by the oxidation of anethoïl, forms colourless needles which melt at 93°. When distilled it decomposes, and is converted into anisic acid, a very small quantity of anisaldehyde being also produced.

Veratrole, under similar conditions, yields *ethylic veratroylcarboxylate;* the acid, which forms colourless crystals melting at 135—136°, has already been obtained by the oxidation of methylisoeugenol.

When distilled in a vacuum, veratroylcarboxylic acid is entirely converted into veratric acid. C. H. B

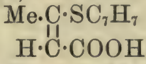
**Isomerism of the Crotonic acids.** By WILHELM AUTENRIETH (*Ber.*, 1896, **29**, 1639—1652).—When the sodium salts of β-chlorocrotonic acid and β-chlorisocrotonic acid are heated with sodium benzyloxide, one and the same *β-benzyloxycrotonic acid* is obtained; the structure of the latter compound is represented by one or other of the following formulæ.

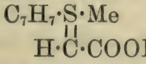


$$\begin{array}{c}\mathrm{Me{\cdot}C{\cdot}OC_7H_7}\\ \|\\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array} \quad \text{or} \quad \begin{array}{c}\mathrm{C_7H_7O{\cdot}C{\cdot}Me}\\ \|\\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}.$$

It crystallises in slender, white needles, and melts sharply at 121·5—122°, decomposing at slightly higher temperatures into carbonic anhydride and β-benzyloxypropylene; it dissolves readily in alcohol, ether, and chloroform, but only sparingly in water; it is not affected by alkalis, but is completely decomposed by warm mineral acids, with the production of acetone, carbonic anhydride, and benzylic alcohol. The *potassium* salt crystallises in white, pearly leaflets.

*β-Benzyloxypropylene*, $CH_2{:}CMe{\cdot}OC_7H_7$, is a thick, colourless oil of agreeable odour, which distils at 191—192° without decomposing, and is volatile in steam; it decolorises bromine water, yielding a reddish oil.

If, in the above experiment, sodium benzylsulphide is substituted for sodium benzyloxide, two isomeric thio-acids are obtained. *β-Thiobenzylisocrotonic acid*,  $\begin{array}{c}\mathrm{Me{\cdot}C{\cdot}SC_7H_7}\\ \|\\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}$, is obtained, together with benzylic bisulphide, when sodium β-chloroisocrotonate is heated in alcoholic solution with sodium benzylsulphide. It may also be prepared by treating a mixture of ethylic acetoacetate and benzylic mercaptan with hydrogen chloride, and then shaking the product with water; the separated oil, ethylic β-dithiobenzylbutyrate, is heated with two molecular proportions of potash, and the resulting potassium salt decomposed by dilute sulphuric acid; the impure β-thiobenzylisocrotonic acid thus obtained is heated in a current of steam until benzylic bisulphide is no longer given off. It crystallises from dilute alcohol in beautiful prisms, and melts at 130—131°, decomposing at slightly higher temperatures into β-thiobenzylpropylene and carbonic anhydride. One part of the acid is dissolved by 30 parts of water at 15°. The *magnesium* salt forms beautiful tabular crystals; the *potassium* and *barium* salts are also described.

*β-Thiobenzylcrotonic aeid*,  $\begin{array}{c}\mathrm{C_7H_7{\cdot}S{\cdot}Me}\\ \|\\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}$, when prepared from β-chlorocrotonic acid in the above manner is accompanied by a large proportion of *β-thiobenzylisocrotonic acid*, the two being separable by means of alcohol, in which the latter is far more readily soluble. When, however, the sodium β-chlorocrotonate is shaken in the cold with sodium benzylsulphide dissolved in alcohol, pure β-thiobenzylcrotonate is obtained. It is insoluble in water, and is less readily soluble than the isomeric acid, both in alcohol and in ether; it dissolves in 131 parts of water at 15°. When heated for a long time in sealed tubes at 130—160°, it is partially changed into its isomeride. Its salts crystallise well, those of *zinc* and *barium* forming pearly leaflets.

*β-Thiobenzylpropylene*, $CH_2\dot{:}CMe\cdot S\cdot C_7H_7$, is produced when either β-thiobenzylcrotonic acid is heated above its melting point. It forms a colourless oil with a disagreeable odour, and boils at about 225°. It is insoluble in water, but miscible in all proportions with alcohol and ether. A. L.

**Perhalogenised Phthalic acids and Hexiodobenzenes.** By Erwin Rupp (*Ber.*, 1896, **29**, 1625—1634).—*Tetrabromoterephthalic acid*, $C_6Br_4(COOH)_2$, is prepared by heating tetrabromoparaxylene for eight hours in sealed tubes at 180°, with potassium permanganate and nitric acid. It crystallises in fine needles, melts and decomposes at 300°, dissolves in alcohol, ether, and acetic acid, but is only very sparingly soluble in cold water and benzene. It may also be prepared by Juvalta's process, namely, by heating terephthalic acid with bromine and fuming sulphuric acid in presence of a little iodine, first at 65°, and finally at 200°; in this case it is accompanied by acids of lower halogen content, and by hexabromobenzene.

*Tetrachloroparaxylene*, $C_6Me_2Cl_4$, is obtained by passing chlorine during three days through a solution of paraxylene in chloroform containing iron dust in suspension; it crystallises from acetic acid in colourless, silky needles, melts at 218°, and dissolves readily in ether, benzene, and hot ethylic alcohol. When oxidised in the above manner, it yields *tetrachloroparatoluic acid*, $C_6Cl_4Me\cdot COOH$, which crystallises in needles, melts at 212°, and, when heated on the water bath with alkaline permanganate, yields *tetrachloroterephthalic acid*, $C_6Cl_4(COOH)_2$. The latter dissolves in alcohol, acetic acid, and ether, but is insoluble in cold water and benzene; it crystallises in long, colourless prisms, and melts at 279—281°; it is also formed from terephthalic acid by Juvalta's process.

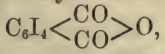
*Tetriodoterephthalic acid*, $C_6I_4(COOH)_2$, prepared from terephthalic acid by the foregoing method, forms colourless needles, melts and decomposes at 315—320°, and dissolves sparingly in acetic acid, ether, benzene, and boiling water. When prepared by Juvalta's process, it is accompanied by acids containing less iodine and by *hexiodobenzene*, $C_6I_6$. The latter is insoluble in all the ordinary media, but may be crystallised from boiling nitrobenzene, when it is obtained as slender, brownish-red needles, which melt and decompose at 340—350°; it is probable that Shaw (Abstr., 1893, 14) was not dealing with this substance.

*Tetrabromisophthalic acid*, $C_6Br_4(COOH)_2$, prepared from tetrabromometaxylene or isophthalic acid, forms colourless needles, melts at 288—290°, and dissolves in ether, acetic acid, and methylic alcohol, but is insoluble in benzene and cold water. *Tetrachlorometatoluic acid*, $C_6Cl_4Me\cdot COOH$, prepared by oxidising tetrachlorometaxylene, melts at 180—181°, and when heated with alkaline permanganate, yields *tetrachlorisophthalic acid*, $C_6Cl_4(COOH)_2$, which forms slender, colourless needles, melting at 267—269°; it dissolves readily in methylic and ethylic alcohol, less readily in ether and acetic acid, and is insoluble in water and benzene. *Tetraiodoisophthalic acid*,

$$C_6I_4(COOH)_2,$$

crystallises in yellow prisms, melts and decomposes at 308—312°, and dissolves in methylic alcohol, but only sparingly in ether, acetic acid, or boiling water.

None of the foregoing substituted phthalic acids are etherified when heated with a 3 per cent. solution of hydrogen chloride in methylic alcohol.

Tetrabromophthalic anhydride is most readily obtained by Juvalta's process. When treated with methylic alcohol and hydrogen chloride, it yields a *monomethylic* salt; this separates from dilute alcohol in silky scales, sinters when heated, melts at 267°, and dissolves readily in benzene, ether and alcohol. *Tetriodophthalic anhydride*,  $C_6I_4<\substack{CO\\CO}>O$, crystallises from acetic acid in lemon-yellow needles, melts at 320—325°, and is nearly insoluble in all ordinary solvents. *Tetriodophthalic acid*, $C_6I_4(COOH)_2$, forms thick needles, melts at 324—327°, and is very sparingly soluble in acetic acid, alcohol, and ether. On etherification by Fisher's process, it yields a minute quantity of the dimethylic salt and a large proportion of *monomethylic salt*. The latter crystallises from acetic acid in sulphur-yellow, shining plates, melts and decomposes at 298°, and dissolves readily in alcohol, ether, and benzene. A. L.

**Formation of Diphenylene Oxide from Phenylic Ether.** By Carl Graebe and F. Ullmann (*Ber.*, 1896, **29**, 1876—1877).—When orthamidophenylic ether (this vol., i, 605) is diazotised, it is converted into a diazo-compound, which is only decomposed very slowly by boiling water—rapidly by boiling 50 per cent. sulphuric acid, diphenylene oxide being formed. Diphenylene oxide is also formed when phenylic ether is passed through a glass tube heated to dull redness. A. H.

**Preparation of Diphenacyl.** By Victor Fritz (*Ber.*, 1896, **29**, 1750—1751; compare this vol., i, 151).—Diphenacyl is best prepared by the action of magnesium powder on an alcoholic solution of bromodiphenacyl. The product contains a little bromine, and must be purified by recrystallisation, a 50 per cent. yield being obtained.
A. H.

**Condensation of Benzophenone Chloride with Benzene and Toluene: Tetraphenylethylene.** By Otto Lohse (*Ber.*, 1896, **29**, 1789—1791).—After quoting Weisse's observation (this vol., i, 565) that triphenylcarbinol chloride does not condense with benzene, &c., in presence of aluminium chloride to form compounds of the type of tetraphenylmethane, and his own (*Diss. Griefswald*) that tetraphenylmethane derivatives are not present among the products of the action of benzophenone chloride, on benzene or toluene in presence of aluminium chloride, the author describes the following results.

When zinc dust is added in small portions to a mixture of benzophenone chloride and a large excess of toluene, the products are tetraphenylethylene, and α- and β-benzopinacoline. If benzene is employed instead of toluene, the reaction is sluggish, and the yield of product small; the reaction may be rendered more brisk, however, by the addition of ether. Tetraphenylethylene may be prepared by the following method, without using metallic silver, as recommended by Behr (this Journal, 1872, 472). Copper-zinc dust, prepared by slowly adding zinc dust (2 mols.) to a slightly acid solution of copper sulphate, is introduced into an ethereal solution of benzophenone chloride, and subsequently a little ethereal hydrogen chloride is added. When the mixture is warmed in a reflux apparatus, a reaction sets in, and tetraphenylethylene is formed, together with the benzopinacolins. If the conditions are such as to preclude the formation of the benzopinacolins, the reaction proceeds very slowly.

A. R. L.

**Menthene and Tertiary Menthol.** By L. MASSON and ALBERT REYCHLER (*Ber.*, 1896, **29**, 1843—1845).—Menthylic chloride prepared from *l*-menthol is added to a hot solution of potash in phenol, and heated for 12 minutes at 150°; on distilling the product, menthene is obtained.

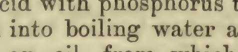
When menthene is heated with trichloracetic acid for half an hour at 70—90°, and the product agitated during 12 hours with potash, tertiary menthol (von Baeyer, Abstr., 1893, i, 722) is produced.

M. O. F.

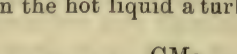
**A Correction [Conversion of Pinene into Camphene].** By ALBERT REYCHLER (*Ber.*, **29**, 1896, 1845—1846).—The author amends his view of the structural changes underlying the conversion of pinene into camphene (compare this vol., i, 313).

M. O. F.

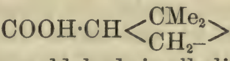
**Orientation in the Terpene Series.** By ADOLF VON BAEYER (*Ber.*, 1896, **29**, 1907—1922; compare this vol., i, 245 and 308).—Pinic acid is shown to contain the group $-\mathrm{CH_2{\cdot}COOH}$ by bromination, conversion of the bromo-acid into hydroxypinic acid (this vol., i, 308), elimination of carbonic anhydride, and oxidation of the aldehyde produced to norpic acid.



*Bromopinic acid*, $\mathrm{COOH{\cdot}CH}{<}\genfrac{}{}{0pt}{}{\mathrm{CMe_2}}{\mathrm{CH_2-}}{>}\mathrm{CH{\cdot}CHBr{\cdot}COOH}$, is obtained by treating pinic acid with phosphorus tribromide and bromine; the product is thrown into boiling water and extracted with ether, the solvent depositing an oil, from which crystals gradually separate. Hydroxypinic acid (*loc. cit.*) is prepared from it by the action of barium hydroxide; copper acetate, which causes no precipitate in a cold solution, produces in the hot liquid a turbidity, which disappears on cooling.

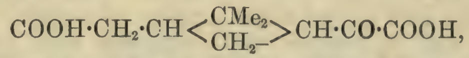


*Norpic acid aldehyde*, $\mathrm{COOH{\cdot}CH}{<}\genfrac{}{}{0pt}{}{\mathrm{CMe}}{\mathrm{CH_2-}}{>}\mathrm{CH{\cdot}COH}$, is formed on adding lead peroxide in small portions to a hot solution of hydroxypinic acid in dilute acetic acid, and is obtained as an oil, which dissolves readily in water, but exhibits no tendency to deposit crystals; the *semicarbazone*, $\mathrm{C_9H_{15}N_3O_3}$, crystallises from hot water in plates, and melts, evolving gas, at 188—189°. The aldehyde gives a metallic mirror with an ammoniacal silver solution, and treatment of the oxime with acetic anhydride, gives rise to a nitrile.

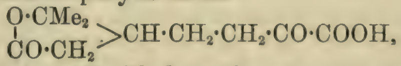


*Norpic acid*, $\mathrm{COOH\cdot CH}{<}\begin{matrix}\mathrm{CMe_2}\\ \mathrm{CH_2}-\end{matrix}{>}\mathrm{CH\cdot COOH}$, is obtained by oxidising the foregoing aldehyde in alkaline solution with a 4 per cent. solution of potassium permanganate; it separates from ether in large, prismatic crystals, and melts at 173—175°, subliming about 100° in needles. The substance is probably identical with the acid $C_8H_{12}O_4$, obtained by Wagner and Ertschikowsky, on treating pinononic acid with alkali hypobromite (this vol., i, 380). In its behaviour towards copper acetate, norpic acid resembles pinic acid, whereas the $\alpha$-pinonic acid yields bluish-green needles on warming the moderately concentrated solution; the *silver* salt crystallises in needles. Boiling acetic chloride does not convert norpic acid into an anhydride, and its stability towards oxidising agents is as marked as that of pinic acid.

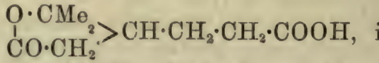
When pinene is oxidised under slightly modified conditions, there is produced along with $\alpha$-pinonic acid a dibasic ketonic acid, derived from the monobasic acid by oxidation of the methylic group attached to the carbonyl radicle; it is named pinoylformic acid, and yields pinic acid on oxidation, whilst hot dilute sulphuric acid converts it into a lactonic acid, bearing to the lactonic isomeride of $\alpha$-pinonic acid the relation in which an $\alpha$-ketonic acid stands to a methyl ketone.



*Pinoylformic acid*, $\mathrm{COOH\cdot CH_2\cdot CH}{<}\begin{matrix}\mathrm{CMe_2}\\ \mathrm{CH_2}-\end{matrix}{>}\mathrm{CH\cdot CO\cdot COOH}$, is separated from the mixture containing $\alpha$-pinonic acid by adding potassium carbonate in quantity insufficient to neutralise the latter acid, which is then removed by extraction with ether; the alkaline liquid containing potassium pinoylformate is acidified, and agitated with ether, the oil obtained on evaporating the solvent being then treated with potassium hydrogen sulphite, and the pinoylformic acid liberated from the resulting compound by means of concentrated barium hydroxide. It is more readily soluble than $\alpha$-pinonic acid in cold water, and crystallises in thin leaflets, which melt at 78—80°; the *silver* salt crystallises in beautiful, lustrous leaflets, which resist the action of light, but copper acetate produces no precipitate in hot or cold solutions of the acid, cuprous oxide being precipitated only when the liquid is boiled for a long time. The *potassium hydrogen sulphite* compound crystallises very readily in aggregates of needles, and the *sodium hydrogen sulphite* compound, which is more soluble in cold water, separates in white leaflets; the *phenylhydrazone* crystallises in flat prisms, and melts, evolving gas at 192·5°. As already stated, oxidising agents convert pinoylformic acid into pinic acid; fuming nitric acid gives rise to oxalic and terpenylic acids.

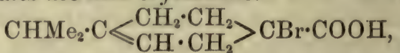


*Homoterpenoylformic acid*, $\begin{matrix}\mathrm{O\cdot CMe_2}\\ |\\ \mathrm{CO\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CH_2\cdot CH_2\cdot CO\cdot COOH}$, is obtained by treating pinoylformic acid with hot, 10 per cent. sulphuric acid; it is sparingly soluble in ether and cold water, and crystallises in prisms, melting at 126—129°. The production of this substance is parallel with the conversion of α-pinonic acid into homoterpenylic methyl ketone (methylethylheptanonolide). On titration with decinormal alkali, homoterpenoylformic acid behaves as a monobasic acid, and the same observation applies to pinoylformic acid; as however, the phenylhydrazone of the latter is dibasic, it is probable that free pinoylformic acid is an acid lactone, the oxygen ring of which is ruptured by phenylhydrazine. Homoterpenoylformic acid resembles pinoylformic acid in behaviour towards copper acetate, but silver nitrate gives no precipitate; the *oxime* crystallises in slender needles, and melts at about 170°, when vigorous liberation of gas occurs.

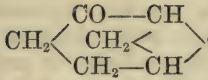
*Homoterpenylic acid*,  $\begin{array}{l}O\cdot CMe_2\\ |\\ CO\cdot CH_2\end{array}\!\!>CH\cdot CH_2\cdot CH_2\cdot COOH$, is obtained from homoterpenoylformic acid alike by lead peroxide and fuming nitric acid; it dissolves somewhat sparingly in cold water, and crystallises in large, lustrous prisms, melting at 98—101°. Ether dissolves it with difficulty, and the crystals from this solvent melt at 100—102·5°. Homoterpenylic acid has to adipic acid the same relation as that in which terpenylic and terebic acids stand to glutaric and succinic acids respectively; it is noteworthy that the relative fusibility observed in the succinic series is reproduced amongst the lactonic derivatives.

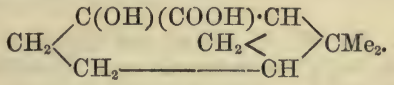
M. O. F.

**Orientation in the Terpene Series. Nopic acid.** By ADOLF VON BAEYER [and VICTOR VILLIGER] (*Ber.*, **29**, 1896, 1923—1929).—Nopic acid is the acidic product of oxidation of French turpentine oil, and is isomeric with α-pinonic acid, but contains no ketonic group (this vol., i, 247). It dissolves with difficulty in water, crystallising from it in long needles, which melt at 126—128°; the sodium salt crystallises in lustrous, rectangular leaflets, and the *potassium* salt, which is more readily soluble in water, resembles it closely. The *barium* and *calcium* salts crystallise in long, slender prisms, and the *silver* salt, which dissolves with extreme difficulty in cold water, forms needles, which resist the action of light; the *copper*, *zinc*, *cadmium*, *manganese*, and *lead* salts are also crystalline.

*Bromotetrahydrocumic acid*,  $CHMe_2\cdot C\!<\!\begin{array}{l}CH_2\cdot CH_2\\ CH\cdot CH_2\end{array}\!\!>CBr\cdot COOH$, is obtained by the action of hydrogen bromide on nopic acid dissolved in glacial acetic acid; it is soluble in chloroform, dissolves sparingly in ether, and is insoluble in petroleum, crystallising in lustrous, rhombic leaflets, which melt, evolving gas at 175°. It decolorises potassium permanganate, and yields silver bromide when treated with boiling aqueous silver nitrate.

*Dihydrocumic acid* is produced by the action of hot, 25 per cent. sulphuric acid on the foregoing substance, which yields the same product under the influence of alcoholic potash; it separates from alcohol in prismatic crystals, and melts at 130—133°. It sublimes at about 100°, and boils at 176° under a pressure of 14 mm.; it dissolves with extreme difficulty in water, but the *sodium* salt is readily soluble, and the *silver* salt crystallises in small needles. The substance reduces a cold, alkaline solution of potassium permanganate, and is oxidised to cumic acid by potassium ferricyanide.

*Nopinone*,  $CH_2\left\langle\begin{array}{l}CO\text{---}CH\\ \quad CH_2 < \quad\\ CH_2\text{---}CH\end{array}\right\rangle CMe_2$, is obtained on passing a current of steam through water in which nopic acid and lead peroxide are suspended; it is a volatile oil of refreshing odour, and is converted by hot, dilute sulphuric acid into a ketone, which is readily oxidised by potassium permanganate. The *oxime* is an oil, and the *semicarbazone* crystallises from methylic alcohol in slender needles, melting at 188·5°. Fuming nitric acid oxidises nopinone, forming homoterpenylic acid, and from this change is deduced the above expression for the constitution of the ketone; the structure of nopic acid is therefore represented by the formula,



$$CH_2\left\langle\begin{array}{l}C(OH)(COOH)\cdot CH\\ \qquad\qquad CH_2 < \\ CH_2\text{————————}CH\end{array}\right\rangle CMe_2.$$

M. O. F.

**Anemonin.** By Hans Meyer (*Monatsh.*, 1896, **17**, 283—299).—Crystallographical measurements of anemonin are given, and our present knowledge of the compound, deducible from this paper and that of Beckurts (Abstr., 1892, 1241) is summarised as follows:—(1) Its formula is $C_{10}H_8O_4$. (2) It yields methyl and ethyl derivatives, which are apparently ethereal salts, showing that it is the anhydride of a dicarboxylic acid. *Dimethylanemonin*, $C_8H_8(COOMe)_2$, melts at 109—110°, *methylanemonin* at 174—176°, *diethylanemonin* at 47°, and *ethylanemonin* at 168—170°. (3) The said dicarboxylic acid is a ketonic acid (*loc. cit.*). (4) By oxidation, anemonin yields succinic and oxalic acids. (5) By hydrolysis of the dialkylic salts before mentioned with alkali and amorphous acid, $C_{10}H_8O_4 + 2H_2O$ is formed, but hydrolysis of them with hydrochloric acid yields a crystalline acid, $C_{10}H_8O_4 + H_2O$ (compare Beckurts, *loc. cit.*). The amorphous acid gives coloured, the crystalline acid colourless, salts. (6) Anemonin is a saturated compound, for by reduction it yields a saturated hydroxy-acid, and absorbs neither chlorine (Hübl solution) nor bromine.

The paper concludes with a discussion of the relative position of the carbonyl to the carboxyl group in anemonin. A. G. B.

**Columbin and Columbic acid.** By Albert Hilger (*J. Pharm.*, 1896 [6], **3**, 299—300; from *Apoth. Zeit.*, 1896, 73).—Columbo roots, in a suitable state of division, are extracted several times with boiling ether. During the cooling, columbin, slightly coloured and contaminated by small quantities of oily matter and of cholesterol, separates. It is merely necessary to wash with cold alcohol and to recrystallise in order to obtain the pure columbin.

The roots are then extracted with 90 per cent. boiling alcohol and finally boiled with dilute milk of lime. The latter extract is filtered, and the filtrate decomposed by means of hydrochloric acid, when columbic acid, mixed with a little berberine and columbin, separates. The acid is best purified by first washing with water until the washings cease to give the reactions for berberine, and finally with boiling ether to remove the columbin.

Columbin, $C_{21}H_{24}O_7$, forms colourless needles, is insoluble in hot and cold water, also in cold alcohol or cold ether, but is readily soluble in boiling ether, chloroform, or alcohol. It melts at 182°, and, when treated with hydrochloric acid, is converted into a monobasic *acid*, $C_{21}H_{24}O_7$. The same acid is formed when columbin is treated with cold dilute alkalis or with hydrobromic or hydriodic acid.

Columbic acid is a yellow amorphous powder, which, after a time, turns brown. It has the characteristic odour of columba root, and is insoluble in water and ether, but readily soluble in cold alcohol. An ammoniacal solution of silver nitrate is reduced in the cold by the acid. It is a monobasic acid, and contains one methoxy-group.

J. J. S.

**Chlorophyll.** By W. A. ALEXANDER TSCHIRCH (*Ber.*, 1896, **29**, 1766—1770).—A reply to Schunck and Marchlewski's criticisms (this vol., i, 574) of the author's previous paper on this subject. All chlorophyll derivatives hitherto examined show an absorption band at H, and this is identical with Soret's blood absorption band in the violet. The purity of the phyllocyanic acid is shown by analysis of three different specimens; no fatty acids could be detected. Phyllopurpuric acid is also homogeneous when prepared by the author's method, which consists in fusing "alkali-chlorophyll" with potash at 210°, dissolving the residue in water, acidifying with hydrochloric acid, and extracting the solution with ether; under these circumstances the ether dissolves only the compound in question, which can readily be obtained in crystals. Schunck and Marchlewski's compound, and that of Hoppe-Seyler, may or may not be identical with this. The fact that phylloxanthin is readily converted into phyllocyanin is no proof that the former is first formed in the leaf extract; the quantity present in solution increases spontaneously if the liquid is kept, and it appears that the reverse change occasionally takes place. The positions of the absorption bands of phyllopurpuric acid and hæmatoporphyrin (two specimens) are fully tabulated according to the author's observations.

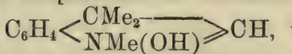
J. B. T.

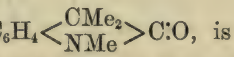
**Stereoisomeric Copellidines. II.** By LUDWIG LEVY and RICHARD WOLFFENSTEIN (*Ber.* 1896, **29**, 1959—1960; compare Abstr., 1895, i, 683).—Copellidine and isocopellidine are separated from each other by treating the mixed hydrochlorides with acetone, which leaves pure copellidine hydrochloride undissolved; the crystalline mixture obtained on evaporating the acetone is spread on porous earthenware, when isocopellidine hydrochloride deliquesces, and may be extracted with acetone after removing the isomeride, which remains on the surface of the plate.

A table included in the paper gives the boiling point, specific gravity, and specific rotatory power of the six stereoisomeric copellidines, along with the melting point of the principal salts.

The authors attribute the isomerism of the copellidines to the relative position, *cis* or *trans*, of the methyl and ethyl groups.

M. O. F.

**An Indolium Base and its Indolinone.** By KARL BRUNNER (*Monatsh.*, 1896, **17**, 253—281; compare this vol., i, 169).—*Isobutylidenephenylmethylhydrazine*, $C_{11}H_{16}N_2$, prepared from isobutaldehyde and phenylmethylhydrazine, was found to be a colourless liquid distilling at 160—163° (48 mm.). In the hope of obtaining a homologue of the hypothetical base $C_{10}H_{11}N$ (*loc. cit.*), this phenylhydrazine was mixed with an alcoholic solution of zinc chloride in an atmosphere of carbonic anhydride, and after five days ether was added; the yellow crystalline powder which separated was treated with potash and shaken with ether; on evaporation of the solvent, 1′ : 3′ : 3′-*trimethylindolium hydroxide*,  $C_6H_4<\begin{matrix}CMe_2\text{—}\\NMe(OH)\end{matrix}\geqslant CH$, was left; this crystallises in colourless, microscopic prisms, melts at 95°, and is very soluble in alcohol, ether, and benzene, less so in light petroleum and in boiling water; it has an odour of thymol and excites sneezing; it volatilises with steam. With a hydrochloric acid solution of the base, ferric chloride gives a yellow precipitate, soluble in alcohol and water. With strong sulphuric acid and a granule of potassium dichromate, it yields an intense brown coloration, which is red if the base has become yellow from exposure to air. The base is a powerful reducing agent. The *hydrochloride* melts at 131°; the *sulphate*, $C_{11}H_{14}N,HSO_4 + H_2O$, melts, when anhydrous, at 129°; the *mercurochloride* melts at 125°, and the *platinochloride* at 161°. The base and its salts are toxic and alkaloïdal in character; the physiological effects are detailed. When boiled with strong hydrochloric acid, the base is converted into Degen's trimethylindole (Abstr., 1887, 149), which melts at 18° and boils at 283—284° (750 mm.). Nitration of the base produces the *dinitro*-derivative, $C_{11}H_{11}(NO_2)_2NO$, which forms yellow crystals and melts at 148°; bromination produces the *dibromo*-derivative, $C_{11}H_{11}Br_2NO$, which crystallises in colourless needles and melts at 126°; reduction with zinc dust produces a crystalline substance, which melts at 129° and has the empirical formula $C_{11}H_{14}N$, but is supposed from its indifferent character to be a bimolecular form, $(C_{11}H_{14}N)_2$.

1′ : 3′ : 3′-*Trimethyl-2′-indolinone*,  $C_6H_4<\begin{matrix}CMe_2\\NMe\end{matrix}>C{:}O$, is prepared by oxidising the indolium hydroxide by boiling its alcoholic solution with an ammoniacal alcoholic solution of silver nitrate; after filtering from the silver and distilling off the alcohol, the oxidation product may be extracted by ether. At first a colourless oil, boiling at 264—265° (751 mm.), it solidifies at low temperatures to crystals which melt at 25°, but if kept at ordinary temperatures these crystals undergo a change and melt at 50°. It has an odour of peppermint, dissolves in organic solvents, and is easily volatile with steam; the *platinochloride*, with $1\frac{1}{2}H_2O$, the *aurochloride*, and the *mercurochloride* (m. p. 122—123°) are described. By bromination, the indolinone yields the same bromine derivative, $C_{11}H_{11}Br_2NO$, as is obtained from the indolium base. By nitration, a *mononitro*-derivative, $C_{11}H_{12}NO{\cdot}NO_2$, is first formed; this melts at 201—202°, and, when further nitrated, passes into the same dinitro-compound as was obtained from the indolium base. It thus seems that the indolium base is first converted into the indolinone by both bromine and nitric acid.

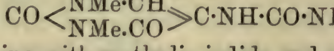
A. G. B.

**Ethylic Quininate and its Conversion into Dihydroxyquinoline.** By FRIEDRICH HIRSCH (*Monatsh.*, 1896, **17**, 327—342).—*Ethylic quininate*, prepared by passing hydrogen chloride into an alcoholic solution of quininic acid, crystallises in colourless needles, melts at 69° (uncorr.), and is insoluble in water; its *hydrochloride* melts at 160° (uncorr.); the *platinochloride* (with $2H_2O$) is described. *Quininamide* crystallises in long, silky, colourless needles, melts at 197°, and dissolves freely in alcohol, sparingly in water and ether, and not at all in benzene and light petroleum; the *hydrochloride* and *platinochloride* are described.

When the amide is treated with potassium hypobromite, it is converted into 3 : 4′-*methoxyamidoquinoline* which crystallises in white needles, and melts at 120°; the *hydrochloride* partly decomposes and melts at 249°, the *platinochloride* at 230°. Through the diazo-reaction, the corresponding 3 : 4′-*methoxychloroquinoline* was prepared; it crystallises in small, colourless, lustrous needles, and melts at 76·5° (uncorr.); the *hydrochloride* melts at 191°, and the *aurochloride* at 177° (uncorr.). The methoxychloroquinoline can be converted into the corresponding *dimethoxyquinoline* by sodium methoxide at 140°, and this into 3 : 4′-*dihydroxyquinoline* by hydrochloric acid at 190°, the latter and its *aurochloride* decompose before they melt. Eleven of the 21 possible dihydroxyquinolines are now known.

A. G. B.

**Hydroxytheophyllin.** By OSKAR WIDMAN (*Ber.*, 1896, **29**, 1954—1956).—The ready conversion of α-acidyl derivatives of phenylsemicarbazide into substituted 3 : 1-hydroxyphenyltriazoles under the influence of dilute alkali, suggested the possibility of obtaining xanthine by this means from hydroxyxanthine. The only result of the action, however, is liberation of ammonia, and production of amidouracil, and a similar experiment with hydroxytheophyllin, the dimethyl derivative of hydroxyxanthine, gave rise to amidodimethyluracil. This method of condensation, therefore, is inapplicable to the compounds in question.

*Hydroxytheophyllin*,  $\mathrm{CO}<\begin{smallmatrix}\mathrm{NMe\cdot CH}\\ \mathrm{NMe.CO}\end{smallmatrix}>\mathrm{C\cdot NH\cdot CO\cdot NH_2}$, is obtained by heating hydroxyxanthine with methylic iodide and sodium methoxide for eight hours at 130—140°; it crystallises from water in small, four sided plates, and when heated evolves gas, but does not melt below 290°. It is insoluble in cold hydrochloric acid, and when evaporated with nitric acid yields a carmine-red residue, which develops a violet coloration with ammonia. When heated with concentrated ammonia for an hour and a half at 140°, it yields a *compound* which crystallises from alcohol in needles, and melts at 163°; in behaviour towards nitric acid it resembles hydroxytheophyllin.

M. O. F.

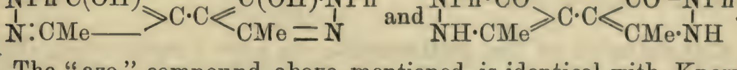
**Lophine and Glyoxalines.** By VICTOR KULISCH (*Monatsh.*, 1896, **17**, 300—308).—In view of Radziszewski's synthesis of lophine and of the formula which he interprets therefrom (Abstr., 1882, 1063), it seemed probable that benzamidine and benzoïn should condense to form an isomeride of lophine. The author finds, however, that lophine itself is the product of the condensation. Ethyllophine (m. p. 234°) yields ethylamine when heated with alcoholic potash, showing that the ethyl group is attached to nitrogen, a conclusion which is confirmed by treating ethyllophine by Herzig and Meyer's method (Abstr., 1895, ii, 296). The same method also showed the presence of ethyl attached to nitrogen in ethylglyoxaline, so that the author concludes that Japp's formula for lophine (Trans., 1882, 323), is correct, and that Radziszewski's formula must be rejected.

A. G. B.

**Action of Phenylhydrazine on the Isomeric Ethylic β-Chlorocrotonates.** By Wilhelm Autenrieth (*Ber.*, 1896, **29**, 1653—1664).—*Ethylic β-chlorisocrotonate* is readily prepared by the action of ethylic alcohol and hydrogen chloride on the corresponding acid. It is a colourless oil of an agreeable odour, and boils at 157—158° under 740 mm. pressure. *Ethylic β-chlorocrotonate*, when prepared in the above manner is obtained unaccompanied by the isomeric salt, and distils at 179—180°.

Phenylhydrazine and either of the foregoing ethylic salts interact at 100° with production of a mixture of substances; this is extracted with ether, which leaves undissolved bis-phenylmethylpyrazolone and phenylhydrazine hydrochloride, whilst the ethereal solution, on evaporation, deposits a mixture of 1 : 3 : 5-phenylmethylpyrazolone, phenylmethylpyrazoloneazobenzene, and the excess of phenylhydrazine.

The above bis-phenylmethylpyrazolone is indentical with that described by Knorr (Abstr., 1884, 1379), the statements extant that this substance is insoluble in alcohol and ammonia being erroneous. When treated with acetic anhydride, it yields but one *diacetyl* derivative, $C_{24}H_{22}N_4O_4$. This crystallises from dilute alcohol in slender needles, dissolves somewhat readily in alcohol, ether, and chloroform, but is insoluble in water; it is not attacked by a boiling solution of sodium carbonate, but is hydrolysed by concentrated potash; it melts at 132—134°. The *dibenzoyl* derivative, $C_{34}H_{26}N_4O_4$, is readily soluble in alcohol, ether, and chloroform, but is not dissolved by water; it crystallises from alcohol in fine needles, and melts at 189—190°. The *disulphonyl* compound, $C_{32}H_{26}N_4S_2O_6$, prepared by adding to a hot alkaline solution of the substance a quantity of benzenesulphonic chloride, crystallises from alcohol in needles, and melts at 190°; it is readily soluble in ether and hot alcohol, sparingly in cold alcohol, and insoluble in water. The production of the foregoing compounds leads the author to propose for bisphenylmethylpyrazolone, the tautomeric formulæ—



$$\begin{array}{l}\mathrm{NPh{\cdot}C(OH)}\\ \mathrm{\,|}\\ \mathrm{N{:}CMe}\text{——}\end{array}\!\!>\mathrm{C{\cdot}C}<\!\!\begin{array}{l}\mathrm{C(OH){\cdot}NPh}\\ \qquad\qquad\;\;|\\ \mathrm{CMe{=}N}\end{array}\quad\text{and}\quad\begin{array}{l}\mathrm{NPh{\cdot}CO}\\ \mathrm{\,|}\\ \mathrm{NH{\cdot}CMe}\end{array}\!\!>\mathrm{C{\cdot}C}<\!\!\begin{array}{l}\mathrm{CO{-}NPh}\\ \qquad\quad\;|\\ \mathrm{CMe{\cdot}NH}\end{array}.$$

The "azo" compound above mentioned is identical with Knorr's 1-phenyl-3-methyl-4-azobenzene, prepared by the interaction of phenylmethylpyrazolone and diazobenzene chloride (Abstr., 1887, 602), and also with the substance obtained by that author (Abstr., 1887, 603) by acting on rubazonic acid with phenylhydrazine. Its production by the interaction of ethylic β-chlorocrotonate and phenylhydrazine is most probably preceded by the formation of ethylic αβ-diphenylhydrazidocrotonate,

$$N_2H_2Ph\cdot CMe\colon C(N_2H_2Ph)\cdot COOEt.$$

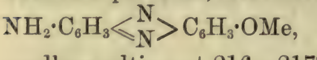
The product, obtained when this substance is treated with nitric acid in the manner described by Knorr (*loc. cit.*), is a mixture of a mononitro- and a dinitro-derivative, which may be separated by means of alcohol. The *mononitro*-derivative, $C_{16}H_{13}N_5O_3$, which is of an orange colour, melts and decomposes at about 234°, is somewhat readily soluble in hot alcohol and chloroform, but is insoluble in water. The *dinitro*-compound, $C_{16}H_{12}N_6O_5$, is of a bright yellow hue, melts and decomposes at 292—294°, and is insoluble in water, alcohol, and ether, but dissolves readily in chloroform. A. L.

**Marcourt's "Formopyrine."** By Friedrich Stolz (*Ber.*, 1896, **29**, 1826—1828).—The substance obtained by Marcourt (*Bull. Soc. Chim.*, 1896, **13**, 520) on allowing antipyrine and formaldehyde to remain together in solution, is identical with methylenediantipyrine (Abstr., 1895, i, 482). This is established by crystallographic comparison of the two compounds, which have the same molecular weight. Pellizzari has quite recently arrived at the same conclusion.

M. O. F.

**Formation of Phenazine.** By Otto Fischer (*Ber.*, 1896, **29**, 1873—1876; compare Abstr., 1893, i, 266).—The synthesis of phenazine derivatives by the action of lead peroxide on amido-compounds succeeds in a large number of cases.

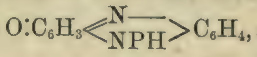
*Orthamidophenyltolylamine* is obtained by the reduction of the corresponding nitro-compound, and crystallises in tablets melting at 76—77°. When its vapour is passed over heated lead peroxide, toluphenazine, melting at 117° is formed. When diamidodiphenylamine [$NH : (NH_2)_2 = 1 : 2 : 4$] is heated with lead peroxide it is at once converted into amidophenazine, although Nietzki and Bauer (this vol., i, 164) were unable to convert this amido-compound into the phenazine derivative.

*Dinitroparamethoxydiphenylamine* is obtained by the action of bromodinitrobenzene on paranisidine. It forms large, pointed, scarlet crystals melting at 141°. On reduction, it yields *diamidoparamethoxydiphenylamine*, which crystallises in colourless tablets melting at 118—120°, and becomes coloured violet on exposure to air. When heated with lead peroxide, it is converted into sym-*paramidomethoxyphenazine*,  $NH_2\cdot C_6H_3\lessdot{}^{N}_{N}\!\!>C_6H_3\cdot OMe$, which crystallises in reddish-yellow needles melting at 216—217°. A. H.

**Constitution of the Safranines.** By Otto Fischer (*Ber.*, 1896, **29**, 1870—1873).—The azonium theory of the constitution of the safranines has been supported by Nietzki (this vol., i, 580), on the ground of the great basicity of many of the compounds in question.

The author finds that aposafranine hydrochloride, diacetylphenosafranine hydrochloride, and acetylaposafranine hydrochloride are all decomposed in dilute solution by dilute soda, the last compound being also decomposed by sodium acetate. The basicity even of true quaternary ammonium bases seems to depend not only on the constitution but also on the other properties of the substance. Thus the products of the action of benzil, $\beta$-naphthaquinone and phenanthraquinone on orthamidodiphenylamine and of $\beta$-naphthaquinone on orthamidoditolylamine are all decomposed by dilute sodium carbonate. A further objection to Nietzki's formula is that it requires the elimination of water between an amido- and an ammonium hydroxide group in the meta-position. A. H.

**Synthesis of Aposafranone (Benzeneindone).** By FRIEDRICH KEHRMANN and H. BÜRGIN (*Ber.*, 1896, **29**, 1819—1820).—When metadinitrophenylorthamidodiphenylamine (Abstr., 1893, i, 199) is heated with benzoic acid until nitric oxide is no longer liberated, *aposafranone*, or benzeneindone (Abstr., 1895, i, 528) is produced; the same substance was originally obtained by Kehrmann and Messinger on heating the foregoing diphenylamine derivative with benzil. It crystallises in lustrous, green needles, and melts at 248—249°; mineral acids give rise to well-defined salts, the hydrochloride forming reddish-brown crystals, but acetic acid does not combine with it. The solution in concentrated sulphuric acid appears green when examined in thin layers, and is purple-red under ordinary conditions.

This method of synthesising aposafranone is further evidence in support of the phenosafranine formula,  $O{:}C_6H_3{<}\genfrac{}{}{0pt}{}{N\text{——}}{NPH}{>}C_6H_4$, already adopted. M. O. F.

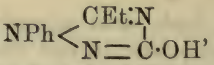
**A Group of 3 : 1-Hydroxyphenyltriazoles.** By OSKAR WIDMAN (*Ber.*, 1896, **29**, 1946—1953).—The production of 3 : 1-hydroxyphenyltriazole by treating phenylsemicarbazide with boiling formic acid (Abstr., 1894, i, 57) has been followed by the observation that $\alpha$-acidyl derivatives of phenylsemicarbazide are converted into substituted hydroxyphenyltriazoles under the influence of 10 per cent. potash at 50°. The compounds thus obtained are distinctly acidic, and also form hydrochlorides, but no platinochlorides; they do not reduce Fehling's solution.

*α-Acetophenylsemicarbazide*, $NPhAc{\cdot}NH{\cdot}CO{\cdot}NH_2$, is prepared from phenylsemicarbazide and acetic chloride dissolved in benzene; it crystallises from alcohol in leaflets, and melts at 196—197°, evolving ammonia. *α-Chloracetophenylsemicarbazide* crystallises in flat needles, and melts at 182°.

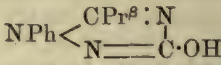
*Phenylglycinylphenylsemicarbazide*,

$$NHPh{\cdot}CH_2{\cdot}CO{\cdot}NPh{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

is obtained from the foregoing compound and aniline, and melts at 202°. *Propionylphenylsemicarbazide*, $CH_2Me{\cdot}CO{\cdot}NPh{\cdot}NH{\cdot}CO{\cdot}NH_2$, crystallises in needles, and melts, evolving gas, at 185—186°.

3 : 1 : 5-*Hydroxyphenylethyltriazole*,  $NPh<\begin{matrix}CEt{:}N\\ N{=}C{\cdot}OH\end{matrix}$, is obtained from propionylphenylsemicarbazide under the influence of 10 per cent. potash; it crystallises from alcohol in long, four-sided prisms, and melts at 191—192°.

*Isobutyrylphenylsemicarbazide*, $CHMe_2{\cdot}CO{\cdot}NPh{\cdot}NH{\cdot}CO{\cdot}NH_2$, dissolves with some difficulty in boiling alcohol, and crystallises in short needles which melt at 219°.

3 : 1 : 5-*Hydroxyphenylisopropyltriazole*,  $NPh<\begin{matrix}CPr^{\beta}{:}N\\ N{=}C{\cdot}OH\end{matrix}$, crystallises from alcohol in slender needles, and melts at 242°; it dissolves readily in ammonia, crystallising from the liquid in long, four-sided prisms. The *hydrochloride* crystallises in beautiful, lustrous prisms, and the *silver* derivative forms small, transparent crystals; the *acetyl* derivative crystallises in rhombic plates, and melts at 93°.

*Butyrylphenylsemicarbazide*, $CH_2Et{\cdot}CO{\cdot}NPh{\cdot}NH{\cdot}CO{\cdot}NH_2$, crystallises in white needles and melts at 184°. 3 : 1 : 5-*Hydroxyphenylpropyltriazole* is obtained from it, and crystallises in rhombic plates which melt at 160°.

*Isovalerylphenylsemicarbazide*, $CH_2Pr^{\beta}{\cdot}CO{\cdot}NPh{\cdot}NH{\cdot}CO{\cdot}NH_2$, crystallises in needles, and melts at 209—210°. It gives rise to 3 : 1 : 5-*hydroxyphenylisobutyltriazole*, which crystallises from alcohol in well-defined rhombohedra, and melts at 164—165°; the *benzoyl* derivative crystallises in four-sided prisms, and melts at 87—88°.

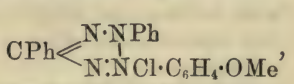
*α-Benzoylphenylsemicarbazide*, $NPhBz{\cdot}NH{\cdot}CO{\cdot}NH_2$, crystallises from alcohol, and melts at 210—211°. 3 : 1 : 5-*Hydroxydiphenyltriazole* is obtained from it, and crystallises in long needles, melting at 290°; the *acetyl* derivative crystallises in four-sided plates or flat needles, and melts at 130—131°.

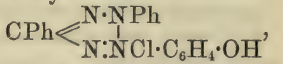
*Cinnamoylphenylsemicarbazide*, $CHPh{:}CH{\cdot}CO{\cdot}NPh{\cdot}NH{\cdot}CO{\cdot}NH_2$, is sparingly soluble in the ordinary media, and crystallises in needles melting at 241—242°. 3 : 1 : 5-*Hydroxyphenylstyryltriazole* crystallises from boiling glacial acetic acid in needles, and melts at 287°; potassium permanganate oxidises it to 3 : 1-hydroxyphenyltriazole (*loc. cit.*), which melts at 273—274°. The *sodium* derivative contains $3\frac{1}{2}H_2O$, and exhibits feeble, yellowish-green fluorescence.

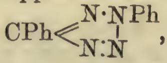
M. O. F.

**Synthesis of Diphenyltetrazole.** By EDGAR WEDEKIND (*Ber.*, 1896, **29**, 1846—1855). The possible occurrence of tautomerism amongst substituted tetrazole derivatives has led the author to synthetise diphenyltetrazole on the lines developed by von Pechmann and Wedekind (Abstr., 1895, i, 574); no indication of the existence of isomeric forms has been observed, and the substance is even more stable than tetrazole.

*Formazylparamethoxybenzene*, $NHPh{\cdot}N{:}CPh{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OMe$, is obtained by cautiously adding alcoholic benzaldehyde and phenylhydrazine, mixed with diazotised para-anisidine, to alcoholic potash, the liquid being vigorously agitated during the operation, which is carried on at 25—35°. On adding alcohol to the solution in chloroform, it separates in green prisms having metallic lustre; it melts at 154°, and develops a magnificent violet coloration with fuming hydrochloric acid.

*Paramethoxytriphenyltetrazolium chloride*,  $\mathrm{CPh}<\begin{array}{l}\mathrm{N{\cdot}NPh}\\ \mathrm{N{:}NCl{\cdot}C_6H_4{\cdot}OMe}\end{array}$, is produced on treating the foregoing compound with amylic nitrite and alcoholic hydrochloric acid. The action of aqueous potassium iodide converts it into the tetrazolium *iodide*, crystallising from water or dilute alcohol in prisms, which melt indefinitely at 135—140°.

*Parahydroxytriphenyltetrazolium chloride*,  $\mathrm{CPh}<\begin{array}{l}\mathrm{N{\cdot}NPh}\\ \mathrm{N{:}NCl{\cdot}C_6H_4{\cdot}OH}\end{array}$, is obtained on heating the methoxy-derivative with concentrated hydrochloric acid for four hours at 150—160°; it crystallises from water in lustrous, yellowish needles, and melts at 243—244°, becoming black. The substance has some of the properties of phenol, bromine water producing a yellow precipitate in dilute solutions, whilst concentrated nitric acid gives rise to a substance resembling picric acid, crystallising in needles which melt at 110—112°. The solutions in alkalis are orange-red, and the sparing solubility of the *nitrate* is very characteristic, the precipitate in dilute solutions resembling silver chloride. Subcutaneous injection causes paralysis of the extremities in rabbits and frogs, ultimately inducing death when administered in doses of 0·16 gram per kilogram weight; the substance, however, appears to undergo no change in the system.

*Diphenyltetrazole*,  $\mathrm{CPh}<\begin{array}{l}\mathrm{N{\cdot}NPh}\\ \mathrm{N{:}N}\end{array}$, is formed on oxidising parahydroxytriphenyltetrazolium nitrate with potassium permanganate; it crystallises from alcohol in colourless, lustrous needles, and melts at 106—107.° It is insoluble in water, but dissolves readily in organic solvents, excepting cold alcohol; it is indifferent towards concentrated nitric acid, but on adding potassium nitrate to the solution in concentrated sulphuric acid at 100°, a white substance is produced which melts at 170°.

*Formazylparahydroxybenzene*, $\mathrm{NHPh{\cdot}N{:}CPh{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH}$, is obtained on reducing parahydroxytriphenyltetrazolium chloride with ammonium sulphide; it sinters at 110°, and melts at 153—155°. The solution in concentrated sulphuric acid is green. M. O. F.

**An Azonium Chloride isomeric with Diphenylfluorindine Dihydrochloride.** By FRIEDRICH KEHRMANN and H. BÜRGIN (*Ber.*, 1896, **29**, 1820—1822).—The *hydrochloride*, $C_{30}H_{22}N_4Cl_2$, is obtained on heating the hydrochloride of the red oxidation product of orthoamidodiphenylamine and the hydrochloride of the base with benzoic acid at 260°, and, after dissolving the product in sufficient boiling alcohol to retain the benzoic acid in solution when the liquid cools, treating it with hydrochloric acid. It crystallises in green needles with metallic lustre, and the solution in water is blue. The substance is isomeric with the dihydrochloride of diphenylfluorindine (this vol., i, 512), which is produced along with it in small quantity. M. O. F.

**Stereoisomeric Coniines.** By RICHARD WOLFFENSTEIN (*Ber.*, 1896, **29**, 1956—1959).—γ-Coniceïne, which is obtained along with coniine from *Conium maculatum*, yields the latter base on reduction with sodium and ethylic alcohol; the modification, however, is optically inactive, and thus a convenient means is afforded of obtaining *i*-coniine.

Ladenburg's isoconiine was stated to form a dimorphous platinochloride, the modifications melting at 175° and 160° respectively (Abstr., 1893, i, 442); the author (Abstr., 1894, i, 627) has shown that the former salt is *d*-coniine platinochloride, and the present communication establishes the identity of the form which melts at 160° with the platinochloride of *i*-coniine. This salt forms bright red, monoclinic crystals, and the axial angle is 64° 30′ (compare Abstr., 1894, i, 307); a parallel crystallographic examination of the platinochlorides from both sources has placed their identity beyond question.

Isoconiine, therefore, is a mixture of dextrorotatory coniine with the inactive modification. M. O. F.

**Glutinpeptones.** By CARL PAAL (*Ber.*, 1896, **29**, 1536; compare the vol., i, 455; *Ber.*, **29**, 1084).—It was previously stated that the deamidonitrosopeptone was easily soluble in methylic alcohol and water, but only slightly soluble in hot absolute methylic alcohol. The latter statement refers to deamidonitrosopropeptone which is almost insoluble in methylic alcohol. J. F. T.

**Deamidoalbumin.** By HUGO SCHIFF (*Ber.*, 1896, **29**, 1354—1356).—In addition to the diamides previously mentioned (this vol., i, 284), tartronamide, dimethylmalonamide, and ethyloxamide give the biuret reaction. Egg albumin, which acts in a similar manner, is converted by the action of sodium nitrite and dilute acetic acid into *deamidoalbumin*, which is a straw-coloured, insoluble compound, containing 14·7 per cent. of nitrogen; that is, about 1 per cent. less than albumin. It does not contain oxides of nitrogen, does not give the biuret reaction, and reacts only slightly, if at all, with Millon's reagent. It is more slowly digested than albumin, and the resulting *deamidopeptone* gives a yellow coloration with copper sulphate and potash, but not the biuret reaction. When albumin is heated with potash (5—6 per cent.) until about 2 per cent. (? of nitrogen) has been evolved as ammonia, the residue gives the biuret reaction only feebly. This deamidopeptone differs from that described by Paal (this vol., i, 455). The author believes that albumin contains both non-basic amido-groups such as $CO{\cdot}NH_2$ and $CS{\cdot}NH_2$, and basic ones (amido-acids), the appearance of the biuret reaction is conditioned by the presence of the former, which, whilst comparatively unstable towards alkali, are almost unaffected by acids, and therefore remain intact in the preparation of Paal's deamidopeptone. J. B. T.

# Organic Chemistry.

**Formation of Gaseous and Liquid Hydrocarbons by the Action of Water on Carbides.** By HENRI MOISSAN (*Compt. rend.*, 1896, **122**, 1462—1467).—Metallic carbides may be divided into two groups, those which are decomposed by water, like the carbides of the alkali and alkaline earth metals, aluminium, and the cerium metals, and those which are not decomposed by water, such as molybdenum, tungsten, and chromium carbides.

The production of gaseous hydrocarbons in all cases in which the carbides are decomposed by water, and the formation of considerable quantities of liquid, and even solid hydrocarbons in some cases (from uranium carbide, for instance), lead to the supposition that similar decompositions may play an important part in the production of natural hydrocarbons, the metallic carbides having been formed in the interior of the earth. It is possible also that certain volcanic phenomena, and especially those eruptions or stages of eruptions in which gaseous and liquid hydrocarbons are evolved, may be due to the sudden contact of water with large masses of metallic carbides.

C. H. B.

**Preparation of Chloroform from Carbon Tetrachloride.** [ANONYMOUS] (*Chem. Centr.*, 1896, i, 362—363; from *L'Union Pharm.*, 1895, 11).—The manufacture of chloroform from carbon tetrachloride can be carried out by heating the latter with zinc and dilute sulphuric acid in an apparatus similar to that used for the manufacture of aniline. The hydrogen chloride which is produced may either be collected and condensed or utilised in the reaction itself; in the latter case, the carbon tetrachloride is treated with zinc and hydrochloric acid in an autoclave without heating.

A. H.

**Acetylene as an Illuminating Agent.** By G. TROUVÉ (*Compt. rend.*, 1896, **122**, 1338—1342).—The author describes portable lamps similar in outward appearance to paraffin lamps, in which acetylene is generated by the action of water on calcium carbide. Provision is made for drying the gas, and the burner is at some height above the generator. Where a large supply of the gas is needed, the generators may be attached to a gas holder of the ordinary form. Two such holders are used, the gas in one being cooled and dried whilst the other is being either emptied or filled, as the case may be. The author attaches considerable importance to the proper cooling and drying of the gas before it is burnt.

C. H. B.

**Double Cyanides.** By RAOUL VARET (*Compt. rend.*, 1896, **123**, 118—119).—The author has extended his researches on the double cyanides (this vol., ii, 513) to those of silver cyanide and nickel cyanide with the cyanides of the alkalis and alkaline earths. For the same group of salts, for example, the compounds of silver cyanide with potassium, sodium, barium, calcium and strontium cyanides, the different members have practically the same heat of formation in a state of solution. Further, none of the compounds can be decomposed by dialysis.

These double cyanides are regarded as salts of complex acids which do not exist in the free state, or else are extremely unstable like hydroargentocyanic acid. J. J. S.

**The Colour of the Alcohols compared with that of Water.** By Walthére Spring (*Zeit. anorg. Chem.*, 1896, **12**, 253—260).—The author has compared the colour of the first members of the series $C_nH_{2n+1}OH$ with that of water. Methylic alcohol is greenish-blue, ethylic alcohol is similar in colour but less intense, and amylic alcohol is greenish-yellow. The pure blue colour of water is gradually more and more mixed with green as one ascends the homologous series. A column of water 26 metres long corresponds in colour with a column 0·314 metre long of a standard 16·32 per cent. copper chloride solution, whilst the colour of a column of methylic or ethylic alcohol corresponds in colour to a column of the copper solution 0·012 or 0·006 metre long respectively. The difference in colour is due to the presence of the carbon chain, and this is clearly seen by comparing the spectra of the compounds. The hydroxyl group absorbs the red rays, and the carbon chain the violet and blue rays, in accordance with the number of the carbon atoms. This is clearly shown in the case of light petroleum, a mixture of the hydrocarbons $C_6H_{14}$ to $C_8H_{18}$; the colour is yellow without the slightest tinge of green, and its spectrum shows only green, orange, and red.

A comparison of the transparency of the compounds gave water = 1, methylic alcohol = 0·98629, ethylic alcohol = 0·98383, amylic alcohol = 0·96576, petroleum = 0·96568. E. C. R.

**Action of Chlorine on Glycerol in Presence of Iodine.** By Al. J. Zaharia (*Chem. Centr.*, 1896, i, 100; from *Bull. Soc. Sci. Fisice*, **4**, 133—136).—When chlorine is passed through glycerol containing iodine, an oil distils over which contains hexachloracetone, boiling at 199—201°. The residue contains trichlorolactic acid, which melts at 124° and boils at 140—170° (pressure = 45 mm.), together with mono- and di-chlorhydrin, oxalic and formic acids, and a substance which reduces Fehling's solution and gives with phenylhydrazine a compound melting at 255°. A. H.

**Tetrallylammonium.** By N. A. Orloff (*Chem. Centr.*, 1896, i, 199; from *Pharm. Zeit. Russ.*, **34**, 755—758).—The aluminium alum of tetrallylammonium loses its water of crystallisation when heated, and then forms a brittle mass which is soluble in water. The aqueous solution gives a red precipitate with a solution of bismuth in potassium iodide. Baryta water produces tetrallylammonium hydroxide, which, like the tetramethyl compound, forms soluble salts with uric acid. The author proposes to use the compound as a solvent for uric acid. The chromium alum of tetrallylammonium has much the same properties as the corresponding aluminium alum. The iron alum could not be obtained.

A note is added to the effect that a good yield of methylic or ethylic iodide can be obtained by the action of potassium iodide and hydrochloric acid on the corresponding alcohol. If sulphuric acid be used, a little granulated zinc should be added. A. H.

**Biuret Compounds.** By HUGO SCHIFF (*L'Orosi*, 1896, **19**, 109—115).—A good yield of biuret is easily obtained by converting carbamide into its hydrochloride with dry hydrogen chloride, heating the product gradually to 130°, aspirating away hydrogen chloride, and extracting ammonium chloride and unaltered carbamide with water; on boiling the residue with 6 per cent. alcoholic potash, all the biuret dissolves, and is partially deposited as *biuret potassium hydroxide*, $C_2H_5N_3O_2,KHO$, on cooling; this crystallises in long needles, is sparingly soluble in hot alcoholic potash, and is decomposed at 90° by water or by the atmospheric carbonic anhydride. The corresponding *sodium* compound, $C_2H_5N_3O_2,NaHO$, is very similar.

On adding mercuric nitrate to a hot aqueous solution of biuret, a white, crystalline *salt* of the composition $C_2H_5N_3O_2,HgO$, is deposited; the mother liquor, on partial neutralisation with potash or potassium carbonate, deposits a caseous, yellow, flocculent *substance* of the composition $Hg(C_2H_4N_3O_2)_2,2HgO$.

Similarly, green, crystalline, copper *compounds*, consisting of $2C_2H_5N_3O_2$ with $CuSO_4$, $Cu(NO_3)_2$, or $CuCl_2$, separate on mixing aqueous or alcoholic solutions of the constituents; these double compounds are dissociated by much water.

On adding concentrated copper acetate solution to biuret potassium hydroxide, and then precipitating with alcoholic potash, a red caseous mass, soon changing into deep red laminæ or long, crimson needles, is deposited; the formation of this substance constitutes the well-known test for biuret. It is very soluble in water, and readily alters in the air; from a study of its formation and decomposition, the author concludes that it has the composition

$$Cu(OH)_2,2KHO,2C_2H_5N_3O_2.$$

The compounds of biuret with nickel salts are analogous to those with copper salts; *compounds* in which $2C_2H_5N_3O_2$ is combined with $NiSO_4$ or $NiCl_2$ have been prepared and analysed.

In order that a diamide shall give the biuret reaction with metallic salts, it seems necessary that it should contain at least two of the groups $-CO{\cdot}NH_2$ combined with each other, or with a single atom of carbon or nitrogen, or with one or more groups $-CO{\cdot}NH-$ existing in an open chain. Thus, the biuret reaction is given by oxamide, hydroxyoxamide, thiobiuret, malonic diamide, tartronic diamide, oxaluramide, oxalyldicarbamide, isosuccinic diamide, dimethylmalonic diamide, and phenyloxamide, but not by oxalyldiureide, carbonyldicarbamide, or succinic diamide. W. J. P.

**Reduction of Nitrates and Formation of Quaternary Nitrogenous Compounds in Plants.** By A. BACH (*Compt. rend.*, 1896,

**122**, 1499—1502).—When formaldehyde is oxidised by nitric acid at 80°, carbonic anhydride, nitrous oxide, nitric oxide, nitrogen, and methylic nitrite are given off, and the liquid contains formaldehyde, methylic alcohol, polymerised trioxymethylene, and ammonium nitrate, with small quantities of methylamine nitrate. Trioxymethylene yields the same products with the exception of methylic nitrite and methylic alcohol. If formaldoxime is formed, it is immediately destroyed. If, however, 5 grams of trioxymethylene is suspended in 100 c.c. of ether, and treated for many hours at 20° with a slow current of nitrogen oxides from sodium nitrite and sulphuric acid, formaldoxime and trioximidomethylene are formed, and give all the reactions described by Scholl (Abstr., 1891, 663). Formamide cannot be isolated from the product of this reaction, but its characteristic mercury compound is formed when formaldehyde is oxidised by nitric acid in presence of mercuric chloride.

Formaldoxime is the first quaternary term of the reduction of nitric acid by formaldehyde, and this fact lends support to the hypothesis that the formation of nitrogen compounds in plants is brought about by the reduction of the nitrates by formaldehyde and the other aldehydic and ketonic derivatives present in the plants.

C. H. B.

**Aliphatic Thiocarbimides.** By GIACOMO PONZIO (*Gazzetta*, 1896, **26**, i, 323—327; compare Abstr., 1895, i, 324).—The author has investigated the fact observed by Hofmann, that in preparing a thiocarbimide by distilling a solution of an alkyl dithiocarbamate with mercuric chloride in a current of steam, twice the theoretical quantity of mercuric chloride has to be used in order to obtain a good yield. The cases investigated were those of the thiocarbamates obtained by the action of carbon bisulphide on propylamine, isobutylamine, isoamylamine, heptylamine, and isoundecylamine. If the theoretical proportion of mercuric chloride be used, hydrogen sulphide is evolved, and never more than a 40 per cent. yield of thiocarbimide is obtained, whilst variable and considerable proportions of the corresponding dialkylthiocarbamide are produced; if, however, twice as much mercuric chloride is used, and the evolution of hydrogen sulphide thus avoided, more than a 90 per cent. yield of thiocarbimide, and no thiocarbamide, are obtained. When the smaller proportion of mercuric chloride is used, it is only natural to conclude that the liberated hydrogen sulphide acts on the alkylthiocarbimide, converting it into the corresponding carbamide and carbon bisulphide. The prevalent opinion that hydrogen sulphide is without action on the aliphatic thiocarbimides is erroneous, for the author finds that, on passing hydrogen sulphide into ethyl-, isobutyl-, and heptylthiocarbimides suspended in water, they are wholly converted into the corresponding thiocarbamides.

*Heptylthiocarbimide*, $C_7H_{15}N{:}CS$, obtained by the general method from heptylamine, is a colourless, very mobile liquid, which is lighter than water, and has a slightly unpleasant odour; it boils at 238° under 732·9 mm. pressure.

*Diheptylthiocarbamide*, $(C_7H_{15}{\cdot}NH)_2CS$, may be prepared by the action of alcohol on heptylammonium heptyldithiocarbamate, or by passing hydrogen sulphide through boiling water containing heptylthiocarbimide in suspension; it is sparingly soluble in water, light petroleum, or alcohol, and crystallises in lustrous scales melting at 58—59°. W. J. P.

**Action of Water on Formaldehyde.** By MARCEL DELÉPINE (*Compt. rend.*, 1896, **123**, 120—122).—Paraformaldehyde, when heated with its own weight of water in sealed tubes at 200°, yields formic acid, methylic alcohol, and carbonic anhydride. These are probably formed according to the equations

$$2CH_2O + H_2O = CH_2O_2 + CH_4O.$$
$$3CH_2O + H_2O = CO_2 + 2CH_2O.$$

A small quantity of carbon monoxide is usually formed by the decomposition of a portion of the formic acid.

If a similar decomposition can be brought about at ordinary temperatures in vegetable tissues, then the author thinks that it would readily account for the presence of free formic acid, and of methylic alcohol in many plants. It also accounts for the fact to which Schloesing (*Compt. rend.*, 1885, **100**, 1237) has drawn attention, namely, the excess of hydrogen over oxygen—as required for a carbohydrate—which exists in most plants. J. J. S.

**Reduction of Crotonaldehyde.** By ER. CHARON (*Compt. rend.*, 1896, **123**, 123—125; compare Lieben and Zeisel, *Monatsh.*, **1**, 823).—On reducing a 10 per cent. solution of crotonaldehyde with a copper-zinc couple in the presence of acetic acid, the author has obtained a mixture of normal butaldehyde, crotonylic alcohol, and the pinacone of crotonaldehyde. The liquid containing the products of reduction is extracted four times with ether, and the ether is carefully evaporated, a Le Bel column being used. The residue is distilled under 20—30 mm. pressure, and the portion which passes over below 115° is freed from acetic acid, and then carefully fractionated at the ordinary pressure; normal butaldehyde (b. p. 75°) first passes over, and finally, between 110° and 122°, the impure *crotonylic alcohol.* The latter is best purified by distillation over quicklime, although this entails a considerable loss of material. As thus obtained, the alcohol is a colourless liquid with a slightly pungent odour; it boils at 122—123°, has a sp. gr. = 0·8726 at 0°, and readily combines with bromine.

The residue, left on distilling off the two above-mentioned products under a pressure of 20—30 mm., is further fractionated under a pressure of 9 mm., when it yields a considerable quantity of a liquid boiling at 120—122°; this is the *pinacone of crotonaldehyde,*

$$CHMe{:}CH{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH{:}CHMe.$$

It readily darkens on exposure to the air, and has a sp. gr. = 0·9833 at 0°. It readily unites with bromine, and yields also a diacetyl derivative. J. J. S.

**Synthesis of Methylheptenone.** By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 1422—1424).—When the amylenic bromide, $CMe_2Br·CH_2·CH_2Br$, is boiled with two molecular proportions of sodioacetylacetone in presence of ether, it yields the compound $CMe_2:CH·CH_2·CH(COMe)_2$ as a colourless, oily liquid; this boils at 112—115° under a pressure of 10 mm. and when treated with concentrated sodium hydroxide solution, splits up into sodium acetate and methylheptenone, $CMe_2:CH·CH_2·CH_2·COMe$.

The methylheptenone thus obtained is identical in all its properties with the natural product from lemon-grass oil and from linaloes, and forms the same semicarbazone melting at 133·5—134°. Since methylheptenone is readily converted into geranic acid (this vol., i, 445), it follows that a complete synthesis of the latter can be made.

In the decomposition of the isoamylacetylacetone by sodium hydroxide, the yield of methylheptenone is small, and the chief product is a ketone, $C_{10}H_{14}O$, which boils at 215—225°.

C. H. B.

**Action of Ethylic Sodacetoacetate on Ethylic β-Bromolevulinate.** By William O. Emery (*J. pr. Chem.*, 1896, [2], **53**, 557—560; compare this vol., i, 414, and Knorr, Abstr., 1886, 331).—By repeating Knorr's experiments (*loc. cit.*), the author has obtained a liquid and a solid ethereal salt; the latter, when purified, crystallises in white needles, melts at 92°, and is soluble in the usual solvents, but not in cold water. Analysis of the salt leads to the formula $C_{13}H_{20}O_6$, but it remains undecided whether

$$COOEt·CH_2·CH(COMe)·CH(COMe)·COOEt$$

or $COMe·CH_2·CH(COOEt)·CH(COMe)·COOEt$ represents the constitution of the compound. When heated with strong hydrochloric acid, the ethereal salt is hydrolysed, and carbonic anhydride is at the same time eliminated, the product being a monobasic acid, $C_8H_{10}O_3$, which melts at 93°. Alcoholic ammonia at 100° converts the ethereal salt into an amide, $C_{11}H_{17}NO_5$. A. G. B.

**Isanic acid.** By Alexandre Hébert (*Compt. rend.*, 1896, **122**, 1550—1553).—The seeds from I'Sano in Loango, known to the natives as *ungueko*, are derived, according to H. Lecomte, from a large tree belonging to the olacineæ. These seeds contain fatty matter which is extracted by benzene and forms a reddish, viscous, rapidly drying oil, which contains 86 per cent. of liquid fatty acids, the lead salts of which are completely soluble in ether. The fatty acids can be separated by fractionally precipitating the mixed ammoniacal salts with barium chloride. They consist of a mixture of 15 per cent. of oleic acid, 75 per cent. of linoleic acid, and 10 per cent. of a new solid acid, which the author calls *isanic acid.* It forms large, flaky crystals, soluble in most organic solvents, and in solutions of alkalis. It has a peculiar odour, is optically inactive, is not volatile in steam, but can be distilled with partial decomposition in a vacuum. When exposed to the air, the acid alters rapidly and absorbs oxygen, with formation of a rose coloured compound which is insoluble in ether, and is very stable. The salts exhibit similar instability. Cryometric determinations show that the acid has a molecular weight of 217, and it seems to have the composition $C_{14}H_{20}O_2$, and to belong to the $C_nH_{2n-8}O_2$ series. It absorbs 2 mols. of bromine, but yields no definite products when heated at 200° with concentrated hydriodic acid. When exposed to light, or when treated with acid mercuric nitrate, it shows no condensation similar to that which occurs with oleic acid.

Ammonium isanate is soluble in water and crystallises in nacreous plates; the barium salt is microcrystalline and dissolves in alcohol and chloroform; the lead and silver salts are amorphous.

C. H. B.

**Succinic and Glutaric acids.** By KARL AUWERS (*Annalen*, 1896, **292**, 132—243).—I.—The author has collected the references in the literature to dicarboxylic acids of the formula $C_7H_{12}O_4$, pointing out that among the 24 possible isomerides, all are known with the exception of tertiary butylmalonic acid, asymmetric methylethylsuccinic acid, and the two $\alpha\beta$-dimethylglutaric acids. Other acids having this formula have been also described, but the second trimethylsuccinic acid and the third symmetrical $\alpha\alpha_1$-dimethylglutaric acid do not exist (Abstr., 1895, i, 505), whilst metapimelic acid, and syrupy trimethylsuccinic acids are impure substances. With regard to isopimelic acid, first obtained by Bauer and Schuler, and subsequently described by Hell and Schad, the author, although unable to adduce direct evidence, is of opinion that this substance is the missing methylethylsuccinic acid.

II. [With F. SCHLOSSER].—Comparative experiments have been made on the relative volatility of substituted succinic and glutaric acids in an atmosphere of steam, the influence of sulphuric acid being also studied. From the tabulated results, which appear in the paper, the following conclusions are drawn. 1. The addition of sulphuric acid increases the volatility, but its influence differs widely among the various acids. 2. Substitution of methyl groups increases the volatility of succinic and glutaric acids. 3. The position of the substituent influences the property in question. 4. Substituted succinic acids are more volatile, and in general considerably more so, than glutaric acids containing the same number of alkyl groups; so marked is this difference that the author regards the property as of value in distinguishing between substituted succinic and glutaric acids, and in this connection points out that camphoric acid is but slightly volatile.

III. 1. [With F. SCHLOSSER].—Diisopropylsuccinic acid is obtained in the form of the ethylic salt by heating ethylic $\alpha$-bromisovalerate with finely divided silver (compare Hell and Mayer, *Ber.*, 1889, **22**, 48); it crystallises from hot water, or dilute alcohol, in long, lustrous needles and prisms, and melts at 180°. It is noteworthy that although symmetrical, disubstituted succinic acids usually occur in two modifications, all attempts to convert diisopropylsuccinic acid into an isomeric modification have hitherto been unsuccessful; another remarkable property of this acid is the electrical conductivity, which is $K = 0{\cdot}3148$, whilst the constants for ethyldimethylsuccinic and propyldimethylsuccinic acids, the highest among the 30 alkylated succinic acids hitherto examined, are 0·0556 and 0·0551 respectively. The anhydride of diisopropylsuccinic acid is a colourless oil which boils at 255—257° under atmospheric pressure, and solidifies in a freezing mixture; it may be heated during several hours with boiling water without undergoing conversion into the acid. The *imide* is obtained by heating the anhydrous ammonium salt in sealed tubes for 6 hours at 230—240°; it crystallises from petroleum in transparent prisms, and melts at 62°. The *anilic acid* crystallises from dilute alcohol in white needles and melts at 179—180°; the *anil* also forms needles, and melts at 95—96°. The *paratolilic acid* and paratolil melt at 172—173° and 113—115° respectively, whilst the *β-naphthilic acid* and *β-naphthil* melt at 164° and 126° respectively. Diisopropylsuccinic acid resists the action of bromine.

III. 2. [With Th. Schiffer and F. Schlosser.]—The *paratolil* of tetramethylsuccinic acid crystallises from dilute alcohol in white needles, melting at 90°; the *β-naphthil*, which also forms needles, melts at 152°. The *benzidine* derivative, $C_{20}H_{22}N_2O_2$, melts at 196°, and the *orthophenylenediamine* derivative crystallises in long, lustrous needles, and melts at 142·5—143°. The *hydrogen methylic* salt crystallises from petroleum in small, white plates, melting at 68°, whilst the *methylic* salt crystallises in prisms, melting at 31°; the *hydrogen ethylic* salt is a viscous oil, which yields ethylic alcohol and tetramethylsuccinic anhydride when heated.

III. 3. [With F. Schlosser].—*Asymmetric methylethylsuccinic acid*, COOH·CMeEt·CH$_2$·COOH, is obtained in the form of its ethylic salt by the action of ethylic sodiomalonate on ethylic α-bromomethylethylacetate, and distillation of the tricarboxylate, thus produced; it crystallises from benzene in lustrous prisms, and when previously dried, melts at 102—103°, the transparent prisms which separate from water melting at the same temperature, and losing water at 190—200°. The electrical conductivity is $K = 0·0248$. The *nickel* salt is a bright green, hygroscopic powder. The *paratolil* crystallises from petroleum in slender, lustrous needles, and melts at 64—65°.

III. 4. [With F. Schlosser].—The electrical conductivity of asymmetric dimethylsuccinic acid is $K = 0·00843$, and it melts at 140—141° (compare Béhal, this vol., i, 179). The *anilic acid* melts at 190—191°, evolving gas (*loc. cit.*) and the *anil* melts at 84—86°; the *paratolilic acid* and *paratolil* melt at 185° and 112—113° respectively, and the *β-naphthilic acid* and *β-naphthil* at 181° and 147—148° respectively.

III. 5. [With J. Harger.]—Compounds analogous to the anils and anilic acids are obtained by the action of secondary bases on succinic anhydride, which also combines with aniline derivatives containing a negative substituent; whilst, however, the anilic acids of the latter class are readily converted into anils under the influence of heat, the corresponding derivatives of secondary bases are resolved into a mixture of succinic acid and tetrasubstituted succinamide.

The *paratolilic acid* melts at 179—180°, and has the same composition as the substance melting at 157° obtained by von Bechi from paratolylsuccinimide under the influence of barium hydroxide; the *paratolil* melts at 151°, and the *paratolylamide* crystallises in nacreous leaflets, and melts at 207°, although according to von Bechi, the melting point is 148°. The *β-naphthilic acid* melts at 184—185°, and the *β-naphthil* at 183°, Pellizzari and Matteucci giving 190—192° and 180°, respectively; the *β-naphthylamide* crystallises in nacreous plates, and melts at 219°.

The *orthonitranilic acid* melts at 132—132·5°, and the *orthonitranil* at 155·5—156°; the *paranitranilic acid* crystallises in lemon yellow needles, and the paranitranil melts at 203—204°. The *orthocarboxyanilic acid*, obtained from succinic anhydride and anthranilic acid, melts at 178°, whilst the *orthocarboxyphenylamide* is an amorphous powder, melting at 191°. The *methylanilic acid*,

$$COOH\cdot C_2H_4\cdot CO\cdot NMePh,$$

melts at 91—92·5°, and the *methylanilide*, $C_2H_4(CO\cdot NMePh)_2$, at 154·5—155°, whilst the *ethylanilic acid* and *ethylanilide* melt at 92—93° and 101—101·5°, respectively. The *diphenylaminic acid*, $COOH\cdot C_2H_4\cdot CO\cdot NPh_2$, melts at 116·5°, and the *tetraphenyldiamide*, $C_2H_4(CO\cdot NPh_2)_2$, at 231°.

IV. 1.—Whilst the formation of anils and anilic acids renders the identification of substituted succinic acids a simple matter, the production of two isomerides surrounds with difficulty the application of this method to asymmetric glutaric acids; the anils, moreover, arising from the latter source, are either unimolecular, having the structure $CH_2<{CH_2\cdot CO \atop CH_2\cdot CO}>NR$, or bimolecular, as represented by the formula $CH_2<{CH_2\cdot CO\cdot NR\cdot CO\cdot CH_2 \atop CH_2\cdot CO\cdot NR\cdot CO\cdot CH_2}>CH_2$. The polymeric anils are less readily fusible than the monomolecular compounds, and the anhydrides of dimethylglutaric acid, already described (Abstr., 1895, i, 210), belong, therefore, to the former class; they resist the influence of hydrolytic agents, and by means of this property may be freed from the unimolecular anils, which are readily converted into the anilic acids.

The general method of preparing the unimolecular anhydrides consists in heating the anilic acid with acetic chloride, whilst the polymerides are most conveniently obtained by boiling the anilic acid in a vacuum for a few minutes.

IV. 2. [With W. Singhof].—The bimolecular paratolil of $\alpha\alpha_1$-dimethylglutaric acid has been already described (*loc. cit.*), and melts at 233°; the *unimolecular paratolil*, obtained by digesting the paratolilic acid with acetic chloride, crystallises from alcohol in prisms and rhombs, both of which melt at 120°.

It has been observed that the anhydride common to the fumaroïd and maleïnoïd forms of $\alpha\alpha_1$-dimethylglutaric acid, yields the latter modification exclusively on hydrolysis, whilst the action of acids on a dibasic metallic salt liberates the particular form from which it is derived; the cyclic *methylenic* and *ethylenic* salts of fumaroïd $\alpha\alpha_1$-dimethylglutaric acid have been therefore prepared. The former salt is rapidly hydrolysed by alcoholic potash, yielding the fumaroïd modification of the acid.

The author has again established the identity of dimethyldihydroxyglutaric acid, obtained by Zelinsky (Abstr., 1892, i, 437), with the product of the action of caustic soda on dibromodimethylglutaric anhydride (Auwers and Jackson, Abstr., 1890, 1098); it crystallises in the triclinic system.

IV. 3. [With W. SINGHOF].—By heating diethyldicarboxyglutaric acid, and also on treating the ethylic salt with sulphuric acid, Dressel obtained a mixture of acids which melted at 63°, and became clear at 100°; this has now been resolved into two isomeric *$\alpha\alpha_1$-diethylglutaric acids.* The less readily fusible form crystallises from water in small prisms, and melts at 118—119°, whilst the electrical conductivity is $K = 0{\cdot}0055$; the isomeride crystallises from petroleum, melts at 76—78°, and has the electrical conductivity $K = 0{\cdot}00595$. The anhydride is an oil which boils at 282—284°, but it is questionable whether this is a homogeneous compound. The *anilic acid* crystallises in silvery needles, and melts at 133—134°, whilst the *paratolilic acid* melts at 179—180°; the *unimolecular paratolil* crystallises from petroleum in prisms melting at 76—82°, and the *bimolecular paratolil* melts at 176—178°.

IV. 4. [With A. W. TITHERLEY].—*Ethylic α-methylcarboxyglutarate*, $CMe(COOEt)_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOEt$, is obtained by the action of ethylic sodiomethylmalonate on ethylic β-iodopropionate; it is a colourless, viscous oil, of sp. gr. = 1·074 at 10·5°, and boils at 164·5—165° under a pressure of 15 mm. When treated with equal volumes of boiling water and concentrated sulphuric acid, evaporated on the water bath, and distilled under diminished pressure, it yields α-methylglutaric acid, which crystallises in prisms, and melts at 77—78°, as already observed. The *anhydride* is a colourless oil, which boils at 272—275° under atmospheric pressure; when heated with aniline in benzene solution, it yields a mixture, from which the *anilic acid* has been isolated; this melts at 114—115°, whilst another modification melts indefinitely at about 100°. The *bimolecular anil* crystallises in slender needles and melts at 175—176°, and the *bimolecular paratolil* and *bimolecular β-naphthil* melt at 170° and 166—169°, respectively; two *paratolilic acids*, melting at 98—99° and 126°, respectively, have been prepared, and the *β-naphthilic acid* melts at 115—119°.

IV. 5. [With A. W. TITHERLEY].—*Ethylic α-ethylcarboxyglutarate*, $CEt(COOEt)_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOEt$, is prepared from ethylic sodioethylmalonate and ethylic β-iodopropionate; it is a colourless, viscous oil, of sp. gr. = 1·059 at 18°, and boils at 180° and 192° under pressures of 25 mm. and 35 mm., respectively. *α-Ethylglutaric acid*,

$$COOH{\cdot}CHEt{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

is obtained from the foregoing salt by elimination of ethylic alcohol and carbonic anhydride, followed by hydrolysis; it separates from petroleum in large crystals, melts at 60·5°, and boils at 194—196° under a pressure of 30 mm. The electrical conductivity is $K = 0{\cdot}005852$. The *anhydride* is a colourless oil, which boils at 275°, and the *anilic acid* and *anil* melt at 154·5° and 167—168°, respectively. The *paratolilic acid*, which melts at 145·5°, crystallises from dilute alcohol in lustrous leaflets, and the *isomeride* melts at 119—120°. The *paratolil* melts at 94—95°, and is therefore probably unimolecular; the *β-naphthilic acids* melt at 129·5° and 142—143°, respectively, and the *β-naphthil* melts at 127·5°.

IV. 6. [With A. W. Titherley].—*Ethylic α-isopropylcarboxyglutarate*, $CPr^{\beta}(COOEt)_2\cdot CH_2\cdot CH_2\cdot COOEt$, is obtained by the action of ethylic sodioisopropylmalonate on ethylic β-iodopropionate, the change proceeding less smoothly than the production of the lower homologues; it is a viscous, colourless oil, of sp. gr. = 1·0567 at 20°, and boils at 197° under a pressure of 33 mm. The *diethylic* salt, $CPr^{\beta}(COOEt)_2\cdot CH_2\cdot CH_2\cdot COOH$, is obtained by heating the triethylic salt with hydrochloric acid during 18 hours; it crystallises from acetic acid in plates, melts at 68—69°, and distils at about 300° without undergoing decomposition.

IV. 7. [With E. Ziegler].—In order to establish the identity of $\alpha\alpha\alpha_1$-trimethylglutaric acid and the non-volatile acid melting at 97° and produced by the action of finely divided silver on ethylic α-bromisobutyrate (compare Hell, this vol., i, 10), the nitrile obtained from mesitonic, or αα-dimethyllevulinic acid, under the influence of hydrogen cyanide, has been submitted to hydrolysis; a lactone is produced, and is converted by hydriodic acid and phosphorus into an acid, which, from its mode of preparation, has the constitution

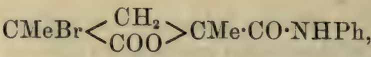
$$COOH\cdot CHMe\cdot CH_2\cdot CMe_2\cdot COOH,$$

and is therefore $\alpha\alpha\alpha_1$-trimethylglutaric acid. This acid is in every respect identical with the substance obtained from ethylic α-bromisobutyrate; the bromanhydride melts at 114°, and the lactonic acid obtained from it at 103—104°. The *anilic acid* crystallises in white needles, and melts at 165°. αββ-Trimethylglutaric acid has been recently obtained by Balbiano (Abstr., 1895, i, 552) and Tiemann (*loc. cit.*, 679).

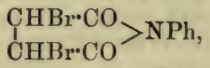
V. [With Th. Schiffer and W. Singhof].—The behaviour of bromocamphoric anhydride towards bases (Abstr., 1893, i, 525) is regarded by the author as evidence in favour of a glutaric formula for camphoric acid, and the action of bases on the anhydrides of bromo-$\alpha\alpha\alpha_1$-trimethylglutaric and symmetrical dibromodimethylglutaric acids has been therefore studied, in order to compare them in this respect with bromocamphoric anhydride; the resemblance between the compounds in question is complete, whilst the anhydrides of isodibromosuccinic and citradibromopyrotartaric acids combine with only one molecular proportion of aniline, forming dibromanilic acids, from which hydrogen bromide is not eliminated spontaneously.

The *anilide* of hydroxytrimethylglutaric lactone,

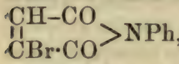
$$CMe_2<\genfrac{}{}{0pt}{}{CH_2}{COO}>CMe\cdot CO\cdot NHPh,$$

is obtained by adding aniline (2 mols.) to the brominated anhydride of $\alpha\alpha\alpha_1$-trimethylglutaric acid, aniline hydrobromide being formed; the anilide crystallises from very dilute alcohol in small, white needles, and melts at 97°. The *amide*, produced when ammonia is employed instead of aniline, melts at 134—135°; its constitution is established by hydrolysis, which converts it into the lactone of hydroxytrimethylglutaric acid. The *anilide* of bromohydroxydimethylglutaric lactone,  $\mathrm{CMeBr}<\begin{matrix}\mathrm{CH_2}\\ \mathrm{COO}\end{matrix}>\mathrm{CMe{\cdot}CO{\cdot}NHPh}$, is obtained by the action of aniline on dibromodimethylglutaric anhydride, and crystallises in lustrous prisms which melt at 137—138°; the *para-toluidide* melts at 172°, and the *β-naphthalide* at 186°.

*Dibromosuccinanilic acid*, $\mathrm{COOH{\cdot}CHBr{\cdot}CHBr{\cdot}CO{\cdot}NHPh}$, is produced on adding aniline to a solution of isodibromosuccinic anhydride (Abstr., 1895, i, 20) in benzene; it crystallises in silky needles, and melts, decomposing, at 144—145°. *Dibromosuccinanil*,

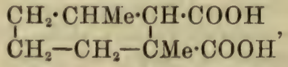


$$\left.\begin{array}{l}\mathrm{CHBr{\cdot}CO}\\ |\\ \mathrm{CHBr{\cdot}CO}\end{array}\right>\mathrm{NPh},$$

is obtained by heating the anilic acid with acetic chloride; it crystallises in lustrous needles, and melts at 177°. *Bromomaleïnanil*,  $\left.\begin{array}{l}\mathrm{CH{-}CO}\\ \|\\ \mathrm{CBr{\cdot}CO}\end{array}\right>\mathrm{NPh}$, is formed when dibromosuccinanilic acid is heated at its melting point; it crystallises in silky needles, and melts at 159—160°, whilst a compound which is formed along with it, crystallises in golden leaflets melting at 200°. *Dibromosuccinoparatolilic acid* melts at 153°, and spontaneously yields *bromomaleïnparatolil*, which crystallises in lustrous, yellowish needles, and melts at 144·5°; *dibromosuccino-β-naphthilic acid* is even less stable than the paratolilic acid.

*Citradibromopyrotartranilic acid* is obtained from aniline and citradibromopyrotartaric anhydride (this vol., i, 131); it crystallises in long, silky needles, and melts at 146°. The *paratolilic acid* also forms needles, and melts at 152°.

VI. [With Th. Schiffer.]—A compound having the constitution expressed by Collie's formula for camphoric acid,



$$\begin{array}{l}\mathrm{CH_2{\cdot}CHMe{\cdot}CH{\cdot}COOH}\\ |\qquad\qquad\quad\ \ |\\ \mathrm{CH_2{-}CH_2{-}CMe{\cdot}COOH}\end{array},$$

should arise from the ethylic salt obtained from ethylic α-bromomethylpropylacetate and ethylic sodioacetoacetate, by intramolecular condensation, followed by hydrolysis and subsequent reduction. A preliminary experiment has been therefore made with ethylic α-bromisobutylacetate, which yields ethylic α-acetyl-$\alpha_1$-isobutylsuccinate by the action of ethylic sodioacetoacetate; the compound obtained by the action of concentrated sulphuric acid on this substance, however, although having the composition $\mathrm{C_{10}H_{14}O_4}$, does not exhibit the properties of an unsaturated dibasic acid, and the attempt to synthesise camphoric acid in the manner indicated has therefore been abandoned.

*Ethylic α-bromisobutylacetate*, $\mathrm{CHMe_2{\cdot}CH_2{\cdot}CHBr{\cdot}COOEt}$, is an oil of agreeable, fruity odour, and boils at 101° under a pressure of 24 mm.; at 202—204°, it distils under atmospheric pressure, a small quantity of hydrogen bromide being eliminated.

*Ethylic α-acetyl-$\alpha_1$-isobutylsuccinate*,

$$\mathrm{CHMe_2{\cdot}CH_2{\cdot}CH(CHAc{\cdot}COOEt){\cdot}COOEt},$$

is a heavy oil, which boils at 161—163° under a pressure of 20 mm.

Under the influence of concentrated sulphuric acid, it yields the *compound*, $C_{10}H_{14}O_4$, which crystallises in small, lustrous needles, and melts at 178—179°; the *phenylhydrazine derivative*, which is not a simple hydrazone or hydrazide, crystallises from alcohol in small, lustrous needles, and melts at 172°. Alkalis convert the compound $C_{10}H_{14}O_2$ into an *isomeride*, a monobasic acid, which crystallises from benzene, and melts at 141—142°; when alcoholic ammonia is employed, this substance is also obtained, together with a nitrogenous compound, melting at 105—106°. M. O. F.

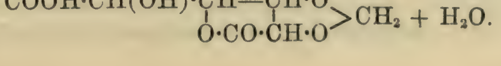
**Action of Formaldehyde and Hydrochloric acid on Tartaric acid.** By W. Henneberg and Bernhard Tollens (*Annalen*, 1896, **292**, 53—55).—*Methylenetartaric acid*, $C_5H_6O_6$, is obtained in small quantity when tartaric acid, formaldehyde, and hydrochloric acid are heated in sealed tubes at 150°; it crystallises from ether in needles containing $\frac{1}{2}H_2O$, and melts at 138—140°. Titration with one-third normal caustic soda indicates that the acid is dibasic.

Crystalline methylene derivatives have not been obtained from mucic acid, *d*-glucose, or isosaccharin. M. O. F.

**Dimethylenegluconic acid.** By W. Henneberg and Bernhard Tollens (*Annalen*, 1896, **292**, 31—39; compare this vol., i, 115).—*Dimethylenegluconic acid*, $C_8H_{12}O_7$, is obtained by heating calcium gluconate with formaldehyde and hydrochloric acid in a reflux apparatus at 110° during an hour; it crystallises in lustrous needles, and melts at 220°. It is somewhat sparingly soluble in water, one part requiring 117·7 parts of the solvent; the specific rotatory power $[\alpha]_D = +41°$. The salts of dimethylenegluconic acid are soluble in water, and the *potassium*, *sodium*, and *ammonium* salts contain $1H_2O$, $1\frac{1}{2}H_2O$, and $2H_2O$ respectively; the *magnesium* salt contains $6H_2O$, and the *calcium* and *strontium* salts $4H_2O$ and $7H_2O$ respectively. The *barium* salt crystallises in octahedra with $4H_2O$; the *copper* salt forms slender, bright blue needles, containing $2H_2O$; whilst the *zinc* and *lead* salts contain $3H_2O$.

Five alternative formulæ are suggested, representing the structure of dimethylenegluconic acid. M. O. F.

**Monomethylenesaccharic acid.** By W. Henneberg and Bernhard Tollens (*Annalen*, 1896, **292**, 40—53).—*Methylenesaccharic acid*, $C_7H_{10}O_8$, is obtained by heating potassium hydrogen saccharate with formaldehyde and hydrochloric acid, in a reflux apparatus, for 1—2 hours at 110°; it separates from a dilute solution in beautiful prisms, sometimes a centimetre long. The acid melts at 144—146°, losing $1H_2O$ at 100°; in the anhydrous state it melts at 176—178°. It dissolves in 41·7 parts of water at 13°, and the specific rotatory power $[\alpha]_D = +117·5°$; its behaviour towards standard alkali is that of a lactonic acid, and the authors accordingly express its constitution by the formula,



$$\begin{array}{l}\mathrm{COOH{\cdot}CH(OH){\cdot}CH{-}CH{\cdot}O}\\ \qquad\qquad\qquad\qquad\ \ \mathrm{O{\cdot}CO{\cdot}CH{\cdot}O}\end{array}\!>\mathrm{CH_2} + \mathrm{H_2O}.$$

It resists the action of 5 per cent. sulphuric acid, and concentrated hydrochloric acid, but becomes yellow when heated with alkalis, formaldehyde being eliminated.

The *sodium* salt crystallises from alcohol, with $2\frac{1}{2}H_2O$; the *potassium* and *ammonium* salts crystallise in needles containing $1H_2O$. The *magnesium* salt contains $1H_2O$, and the *calcium* salt, which crystallises in microscopic, six-sided plates, contains $4H_2O$; the *strontium* and *barium* salts, $4H_2O$; the *copper* salt, $2H_2O$, and the *zinc* salt, $3H_2O$; whilst the *lead* salt is anhydrous. The *ethylic* salt crystallises in long, slender needles, and melts at 192—194°, and when treated with hot, one-third normal, caustic soda, neutralises a quantity of the agent which indicates rupture of the lactone ring.

M. O. F.

**The Benzene Nucleus.** By WILHELM VAUBEL (*J. pr. Chem.*, 1896, [2], **53**, 549—557; compare Abstr., 1895, i, 53, 339; this vol., i, 213, 352).—From a review of the behaviour of the dinitrobenzoic acids and of the nitro- and dinitro-phthalic acids with tin and hydrochloric acid, it is concluded that by this treatment (1) an elimination of the carboxyl group does not occur when there is a nitro-group or a second carboxyl group in the meta-position to the carboxyl group; and (2) in the absence of such a protective group an elimination of the carboxyl group will only occur when two negative groups occupy the ortho-positions, or the ortho- and para-positions relatively to the carboxyl group. These observations are discussed in connection with the author's benzene configuration (Abstr., 1894, i, 325).

The bromination of asymmetrical acetometaxylidine yields a bromo-derivative, which melts at 95—96°, whilst the acetylisation of the bromoxylidine (m. p. 45°) obtained by brominating asymmetrical metaxylidine yields a compound which melts at 193°. This fact, which escaped the notice of Wroblewski (*Annalen*, 1878, **192**, 215), is here explained by the author's configuration for benzene.

The paper concludes with some remarks on the decomposition of the phenolcarboxylic acids in presence of aromatic bases as elucidated by Cazeneuve (*Chem. Centr.*, 1896, i, 494).

A. G. B.

**Action of the Chlorides of Phosphorus on Halogenised Phenols.** By AL. J. ZAHARIA (*Chem. Centr.*, 1896, i, 100); from *Bull. Soc. Sci. Fisisce*, **4**, 130—135).—A mixture of trichlororesorcinol with phosphorus trichloride reacts with phosphorus pentachloride at 250—280°, with formation of pentachlorobenzene, according to the equation, $C_6HCl_3(OPCl_2)_2 + 2PCl_5 = C_6HCl_5 + 2POCl_3 + 2PCl_3$; a certain amount of hexachlorobenzene is also formed. Trichlorophenol, when treated in a similar manner, yields 1 : 2 : 4 : 6-*tetrachlorobenzene*, melting at 54—55°, and *hydrogen trichlorophenylic phosphate*, $(C_6H_2Cl_3O)_2PO{\cdot}OH$, which melts at 230°; the latter can only be hydrolysed with difficulty, and yields numerous salts. The *methylic salt* melts at 132—133°.

A. H.

**Two Isomerides of Anethoïl.** By CHARLES MOUREU (*Compt. rend.*, 1896, **123**, 57—60).—The author has prepared *orthopropenylanisoïl* and the corresponding *meta-compound*, both of which are isomeric with anethoïl (parapropenylanisoïl). They were obtained by heating a mixture of propionic anhydride and dry sodium propionate with ortho- and meta-methoxybenzaldehyde respectively. *Orthanethoïl* (orthopropenylanisoïl), $OMe{\cdot}C_6H_4{\cdot}CH{\colon}CHMe$, is a liquid with an odour resembling that of veratrole; it boils at 220—223°, has a sp. gr. = 1·0075 at 0°, does not solidify at −23°, and readily unites with 2 atoms of bromine.

*Metanethoïl* boils at 226—229°; its sp. gr. at 0° is 1·0013, and it also readily combines with 2 atoms of bromine. Orthomethoxyphenylcrotonic acid, m. p. 107—108° (compare Perkin, Trans., 1881, **39**, 431, 446 and 449), and *metamethoxyphenylcrotonic acid*, $OMe{\cdot}C_6H_4{\cdot}CH{\colon}CMe{\cdot}COOH$, may be respectively isolated from the two residues after distilling off the corresponding anethoïls in a current of steam. The meta-acid, which is new, crystallises in long, brilliant needles, melts at 92—93·5°, and is sparingly soluble in boiling water. J. J. S.

**Dehydrothiotoluidine; Primuline Base.** By WILHELM VAUBEL (*J. pr. Chem.*, 1896, [2], **53**, 548—549).—The accepted constitution of dehydrothiotoluidine (Abstr., 1889, 867) leads to the expectation that the compound should combine with 2 atoms of bromine, since it contains an amido-group and two unoccupied ortho-positions. As a fact, the addition of a solution of potassium bromide and bromate to a solution of the base in glacial acetic and hydrochloric acids causes the separation of an orange *dibromo*-derivative melting at 184° (uncorr.). Primuline base, however, does not combine, or combines very slowly, with nascent bromine. A. G. B.

**Action of Acid Hydrazides on Acid Azides.** By THEODOR CURTIUS and T. S. HOFMANN (*J. pr. Chem.*, 1896, [2], **53**, 513—531).—Acid hydrazides generally react with acid azoimides to form symmetrical diacidylhydrazines, hydrogen nitride being eliminated (Abstr., 1894, i, 331); but when the action occurs in boiling acetone, a carbamic acid derivative (a semicarbazide) is the product, and nitrogen is set free. The constitution of the compounds, obtained in this way from benzoylazoimide, is settled by their behaviour on hydrolysis by acids, when they are resolved into aniline salts, carbonic anhydride, a hydrazine salt, and an acid corresponding with the acid radicle.

*Phenylbenzoylsemicarbazide*, $NHPh{\cdot}CO{\cdot}NH{\cdot}NHBz$, is prepared by heating for six hours in a reflux apparatus a mixture of benzoylazoimide with benzohydrazide in molecular proportion dissolved in acetone. It forms colourless, lustrous crystals, melts at 212°, and dissolves freely in alcohol and glacial acetic acid, sparingly in hot water, benzene, acetone, and chloroform, but not in cold water. Hydrolysis with acids converts it into aniline, carbonic anhydride, hydrazine, and benzoic acid.

*Phenylmetanitrobenzoylsemicarbazide*, prepared in like manner from benzoylazoimide and metanitrobenzohydrazide, crystallises in yellowish laminæ, melts at 204°, and dissolves in hot glacial acetic acid or hot alcohol, sparingly in acetone and chloroform, and hardly at all in ether or benzene.

*Metanitrophenylbenzoylsemicarbazide*, from metanitrobenzoylazoimide and benzohydrazide, is a yellowish, crystalline powder which melts at 226°, and is more sparingly soluble in alcohol than is the last-named compound, although it shows about the same solubility in other solvents. Both these compounds behave normally on hydrolysis (see above).

*Phenylacetylsemicarbazide*, $NHPh\cdot CO\cdot NH\cdot NHAc$, is prepared by dissolving 125 grams of benzoylazoimide in acetone, drying the solution over calcium chloride, and adding 100 grams of acetonylacethydrazide dissolved in much acetone; the mixture is boiled in a reflux apparatus for 10 hours, the acetone then evaporated, and the cooled residue dissolved in hot water. The filtered solution, as it cools, deposits the new compound in white laminæ or needles; it melts at 171·5°, and dissolves freely in alcohol, also in hot benzene, acetone, hot chloroform, glacial acetic acid, and hot water. By its hydrolysis, *phenylsemicarbazide*, $NHPh\cdot CO\cdot N_2H_3$ (isomeric with E. Fischer's compound, Abstr., 1878, 307), may be obtained as an intermediate product; this can be isolated as its benzylidene derivative, which may be subsequently decomposed by boiling hydrochloric acid, the liberated benzaldehyde being extracted by benzene, and the hydrochloric acid solution concentrated to obtain the crystalline phenylsemicarbazide hydrochloride. The base crystallises from hot water in colourless, lustrous laminæ, melts at 122°, and dissolves freely in alcohol, chloroform, and hot benzene, but not in ether; alkalis and acids dissolve it, the latter forming red salts; it reduces Fehling's solution and ammoniacal silver nitrate. The *hydrochlorides*, $NHPh\cdot CO\cdot N_2H_3,2HCl$ and $NHPh\cdot CO\cdot N_2H_3,HCl$, are described; the former is reddish, but becomes colourless at 190°, and melts at 213°. The *benzylidene* derivative (m. p. 174°), the *orthohydroxybenzylidene* derivative, and the *cinnamylidene* derivative are described. *Acetonylphenylsemicarbazide*, $NHPh\cdot CO\cdot NH\cdot N{:}CMe_2$, from acetone and phenylsemicarbazide, crystallises in colourless needles, melts at 155—156°, and dissolves freely in alcohol, acetone, benzene, and chloroform, but only very sparingly in water.

*Phenylcarbamazide*, $NHPh\cdot CO\cdot N_3$, prepared by diazotising phenylsemicarbazide, crystallises in colourless needles, melts to a red liquid at 103—104°, and dissolves freely in ether, alcohol, acetone, benzene, and chloroform, but not in water; it is volatile with steam, and has a burning taste; its behaviour with boiling water is described, but requires further investigation.

A prescription for the preparation of acethydrazide in quantity is given in the paper; it melts at 67° (Abstr., 1895, i, 263). *Acetonylacethydrazide* crystallises in white needles and melts at 133°.

A. G. B.

**Permanency of Pigments on Cotton-fibre.** By V. N. Oglobin (*J. Russ. Chem. Soc.*, 1894, **26**, 107—136).—A long series of inorganic, organic, and vegetable pigments fixed on cotton fibre has been subjected to the action of sunlight during 366 days with a view of ascertaining the character of the alteration which the pigments undergo, the part played by oxygen and by moisture in decolorisation, also the effect of the separate rays of the spectrum, and, lastly, the behaviour of the decolorised pigments to different chemical reagents. The results arrived at at present may be summarised as follows: (1) Mineral pigments are the most permanent, except manganic peroxide which is partly bleached after one year. (2) Aniline black is very permanent, remaining unaltered after a year's exposure. (3) The pigments derived from anthracene either remain entirely unaltered after a year's exposure, or acquire a slightly different shade of colour which, however, is very permanent. (4) The rosaniline group is altered by strong sunlight in three days; entirely decolorised in 200 days. (5) The phthaleïns and most of the azo-compounds, when applied as pigments, are similarly fugitive, but when developed on the fibre they are much more permanent. (6) Dyes of the diphenylamine series are intermediate in permanency between the anthracene and the rosaniline groups. (7) The permanency of vegetable dyes depends almost entirely on the character of the mordant, and, if well fixed, they rank immediately after the anthracene derivatives in stability. S. G. R.

**Preparation of Aldehydes of the Benzene Series.** By LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 1543—1545).—When glyoxylic acids are heated with aniline at its boiling point, they are converted into phenylimido-acids, which at once decompose into carbonic anhydride and phenylimides.

These phenylimides are very stable, and can be distilled under diminished pressure without decomposing, but when boiled with dilute sulphuric acid, they readily yield aniline and pure aldehydes.

Metaxylylglyoxylic acid yields a phenylimide which boils at about 190° under a pressure of 10 mm. The 2 : 4-*dimethylbenzaldehyde* obtained from it boils at 99° under a pressure of 10 mm., yields a hydrazone melting at 114°, and forms 2 : 4-*dimethylbenzoic acid* melting at 125°.

Cymylglyoxylic acid, from camphor cymene, yields *methylpropylbenzaldehyde*, $C_{11}H_{14}O$, which boils at 120° under a pressure of 10 mm., and forms a hydrazone melting at 133°. It has the constitution

$$[\mathrm{CHO : Me : Pr} = 1 : 2 : 5 \text{ or } 1 : 3 : 6].$$

Anisoylcarboxylic acid yields anisaldehyde, and veratroylcarboxylic acid yields a phenylimide, which boils at 235° under a pressure of 10 mm., and is readily converted into veratraldehyde (methylvanillin).

The glyoxylic acid from metadimethoxybenzene melts at 106°, its phenylimide boils at 245° under a pressure of 10 mm., and the *metadimethoxybenzaldehyde* [CHO : OMe : OMe = 1 : 2 : 4] melts at 66°, and boils at 165° under 10 mm. Paradimethoxybenzene yields dimethylgentisaldehyde, which boils at 146° under 10 mm. pressure, and forms acicular crystals, which melt at 51°. C. H. B.

**Electrolytic Reduction of Benzaldehyde.** By H. KAUFFMANN (*Chem. Centr.*, 1896, i, 101; from *Zeits. Elektrotechn. und Elektro-*

*chemie*, 1895, 365—367).—When a solution of benzaldehyde in potassium hydrogen sulphite solution is electrolysed with a current of 0·8 ampère and 6—7 volts, using a platinum cathode of 130 square cm. area, hydrobenzoïn and isohydrobenzoïn are formed. The same products are obtained when the aldehyde is simply covered with a little aqueous soda and then electrolysed, whereas, in the presence of sulphuric acid, nothing but a tarry mass is formed. A. H.

**Action of Hydrazine on the Glyoxylic acids of the Benzene Series.** By Louis Bouveault (*Compt. rend.*, 1896, **122**, 1491—1493).—The glyoxylic acids react with hydroxylamine, and yield oximes, but when the latter are heated, they lose water, and yield nitriles instead of the oximes of the corresponding aldehydes.

If, however, the sodium salts of the glyoxylic acids are boiled with hydrazine sulphate solution, they yield crystalline yellow acids slightly soluble in boiling water, but almost insoluble in neutral solvents. They all contain $1H_2O$, which they do not lose at 100°, and have the general formula $COOH{\cdot}CR{:}N{\cdot}N{:}CR{\cdot}COOH + H_2O$. When carefully heated, they lose water at about 150°, and at a higher temperature carbonic anhydride is evolved, decomposition being complete after heating for an hour at 180—220°. The hydrazones, $CHR{:}N{\cdot}N{:}CHR$, thus produced crystallise readily, and are usually yellow. Those derived from the simpler hydrocarbons can be distilled under diminished pressure without decomposing, but if distilled at the ordinary pressure, they all yield nitrogen and substituted stilbenes, and the reaction can be applied to the preparation of various stilbenes.

Sulphuric acid of 15 per cent. has no action on these hydrazones at its boiling point, but when heated in sealed tubes at 140—150°, the hydrazones are converted into hydrazine sulphate and aldehydes, the yield, however, is poor.

Phenylglyoxylic acid yields hydrazonephenylglyoxylic acid, which melts and decomposes at 179° with formation of the benzylidenehydrazone described by Curtius. Paracresylglyoxylic acid forms a hydrazone which melts at 200°, and yields the hydrazone of paratolualdehyde; the latter, when distilled under atmospheric pressure, yields paradimethylstilbene. Anisoylglyoxylic acid yields a hydrazone acid, which, in its turn, yields the hydrazone of anisaldehyde, melting at 168°, and a small quantity of an isomeride which dissolves in ether and melts at 152°; it is the hydrazone of metamethoxybenzaldehyde. Veratroylgloxylic acid yields a hydrazone which melts and decomposes at 184°; the hydrazone of veratraldehyde melts at 190°. C. H. B.

**Combination of Antipyrine with the Hydroxybenzoic acids and their Derivatives.** By Gustave Patein and E. Dufau (*Compt. rend.*, 1896, **122**, 1335—1338).—Parahydroxybenzoic acid, like salicylic acid, readily combines with antipyrine, forming a compound of the composition $C_7H_6O_3,C_{11}H_{12}N_2O$, which crystallises from water or alcohol, does not alter when exposed to air, and melts at 78—82°. With ferric chloride, it gives the antipyrine reaction. Metahydroxybenzoic acid yields an analogous compound, which, however, is liquid.

Sodium salicylate seems to form an unstable compound with antipyrine, but no combination takes place between the latter and methylic salicylate. Anisic acid (paramethoxybenzoic acid) likewise does not combine with antipyrine. Saligenin, on the other hand, yields the compound $C_7H_8O_2,C_{11}H_{12}N_2O$, which is an oily liquid.

Saligenin is a phenol-alcohol, and from the other known facts concerning the reactions of antipyrine with simple and mixed phenols, the conclusion is drawn that it is the phenolic hydroxyl and not the carboxylic hydroxyl of the hydroxybenzoic acids that determines their combination with antipyrine. C. H. B.

**Dichlorogallic acid and Trichloropyrogallol.** By ALEXANDRE BIÉTRIX (*Compt. rend.*, 1896, **122**, 1545—1548).—When an aqueous solution of gallic acid is treated with chlorine, it is completely oxidised, and the chief product is oxalic acid; dibromogallic acid behaves similarly. In presence of alcohol, the reactions are very complex. If, however, the gallic acid is dissolved in about five times its weight of chloroform, and treated with excess of chlorine, it yields dichlorogallic acid, which is insoluble in chloroform, and a small quantity of trichloropyrogallol, which remains in solution.

Dichlorogallic acid crystallises from sulphurous acid in large, white, prismatic crystals very soluble in alcohol or ether, but insoluble in benzene as well as in chloroform. It becomes brown at 180°, and melts and decomposes at 190°. The crystals contain $2H_2O$, and effloresce in a vacuum. Solutions of the acid give a blue coloration with ferric chloride and a rose coloration with alkalis, less intense than that given by dibromogallic acid. Lime water and baryta water give a blue coloration changing to rose.

Trichloropyrogallol crystallises from water in slender needles, which melt and decompose at 178°, and dissolve readily in alcohol and ether. The crystals contain $3H_2O$, which they lose in a vacuum. The triacetyl derivative melts at 125° without decomposing.

C. H. B.

**Action of Chlorine on Benzoylnitrocarbazole.** By MANFREDO LAMBERTI-ZANARDI (*Gazzetta*, 1896, **26**, 289—293; compare this vol., i, 304).—The benzoylnitrocarbazole, melting at 181°, can be chlorinated in a boiling, dry chloroform solution in presence of iodine, and, after evaporating off the solvent, washing with alkali carbonate, and crystallising from acetic acid, a *benzoylnitrochlorocarbazole*, $C_{19}H_{11}ClN_2O_3$, is obtained, which crystallises in minute, yellow needles melting at 257—258°; it is soluble in benzene or toluene, but only sparingly so in alcohol. It is hydrolysed by boiling alcoholic potash with formation of a *nitrochlorocarbazole*, $C_{12}H_7Cl(NO_2)N$, which crystallises in thin, yellow needles melting at 285—286°, and is soluble in toluene or alcohol.

*Acetylnitrochlorocarbazole*, $C_{12}H_6Cl(NO_2)NAc$, is obtained by heating nitrochlorocarbazole with acetic anhydride at 170—180° for six hours; it crystallises in white needles melting at 205—206°.

W. J. P.

**Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Naphthalene in the presence of Aluminium Chloride.** By L. Rousset (*Compt. rend.*, 1896, **123**, 60—62; compare Bouveault, this vol., i, 551, 616).—Ethylic chloroglyoxylate reacts with naphthalene in the presence of aluminium chloride to form a mixture of ethylic α- and β-naphthylglyoxylates; these are best separated by treating a solution of the two in methylic alcohol with picric acid, the α-glyoxylate uniting with the picric acid to form a definite compound, which crystallises in yellow needles, and melts at 77°. When decomposed with sodium carbonate, this picrate yields *ethylic α-naphthylglyoxylate;* this is a viscid liquid, boiling at 213—215° under a pressure of 23 mm., and having a sp. gr. = 1·19 at 0°. On hydrolysis it yields *α-naphthylglyoxylic acid*, which readily crystallises from benzene; these crystals, which contain benzene, turn brown at 95° and melt at 100°; when free from benzene, the acid melts at 107—108°. Compare Claus and Feist (Abstr., 1887, 271), who give the melting point of the acid as 113·5°. The acid yields an *oxime* melting and decomposing at 193—195°; this when distilled under diminished pressure, decomposes, yielding α-naphthonitrile, which melts at 34°, boils at 170—175° under a pressure of 20 mm., and yields a *picrate* melting at 97°.

Ethylic β-naphthylglyoxylate boils at 212—215° under a pressure of 20 mm.; its sp. gr. at 0° = 1·18. No pure derivatives could be obtained.

The two naphthylglyoxylic acids, when heated with aniline, yield phenylimides, and these, when boiled with dilute sulphuric acid yield the naphthoic aldehydes, which have already been described by Bamberger and Lodter (Abstr., 1888, 375), Battershall (*Annalen*, 1883, **168**, 116), Schulze (Abstr., 1884, 1184), and Bamberger and Böckmann (Abstr., 1887, 675). J. J. S.

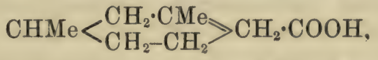
**Camphorpinacone.** By Ernst Beckmann [and Aug. Stock] (*Annalen*, 1896, **292**, 1—30; compare Abstr., 1894, i, 614).—Camphorpinacone, $C_{20}H_{34}O_2$, crystallises in pyramids belonging to the rhombic system; $a : b : c = 0·9573 : 1 : 1·1035$. It melts at 157—158°, is odourless and tasteless, and is very slightly volatile in an atmosphere of steam; in a solution containing 23 grams of the pinacone in 100 grams of benzene, the specific rotatory power $[\alpha]_D = -27·3°$.

Whilst the foregoing substance is obtained from dextro-camphor, reduction of lævo-camphor gives rise to an *isomeride* which, in benzene solution, has the specific rotatory power $[\alpha]_D = +26·5°$.

The author describes in some detail the substances already enumerated (*loc. cit.*), and develops a system of nomenclature applicable to them; the constitution of the more prominent compounds is also discussed. M. O. F.

**Constitution of Inactive Campholenic acid.** By Guerbet and Auguste Béhal (*Compt. rend.*, 1896, **122**, 1493—1496).—When heated in a sealed tube with bromine, inactive campholenic acid yields Claus' metaxylylacetic acid (Abstr., 1890, 979) which, however, melts at 106°, boils at 300—302° (corr.), and yields an amide melting at 183°.

It follows that campholenic acid is tetrahydrodimethyl-1 : 3-phenethyloic-4-acid (tetrahydropseudocumenecarboxylic acid)



$$CHMe{<}\begin{matrix}CH_2{\cdot}CMe\\CH_2{-}CH_2\end{matrix}{>}CH_2{\cdot}COOH,$$

though there is some uncertainty as to the position of the ethylenic grouping. This view is inconsistent with the results of the oxidation of campholenic acid (this vol., i, 55, 179), although it agrees well with all other transformations (Abstr., 1895, i, 240, 241, 552, 623). It is, however, known that in several instances oxidation is accompanied to some extent by molecular transformations, and it seems probable that such changes take place in the oxidation of campholenic acid. Since this acid contains an ethylenic group, it may possibly be first converted into a pinacone, which is converted into a pinacoline, the latter being subsequently oxidised with transposition of a methyl group.

C. H. B.

**Camphoronic acid.** By JULIUS BREDT [and in part E. ARNTZ and ALFRED HELLE] (*Annalen*, 1896, **292**, 55—132; compare Abstr., 1895, i, 242).—The author states that camphoronic acid melts at 136—137°, and confirms the observation of Hess (this vol., i, 102); anhydrocamphoronic acid melts at 139°, and crystallises in the rhombic system, $a : b : c = 0{\cdot}96887 : 1 : 0{\cdot}80866$.

The paper is devoted to a detailed account of derivatives of camphoronic acid already described (Abstr., 1895, i, 242), and the author discusses the question of constitution at considerable length.

M. O. F.

**Red Pigment from Amanita muscaria.** By ARTHUR B. GRIFFITHS (*Compt. rend.*, 1896, **122**, 1342).—The red pigment of *Amanita muscaria* (*Agaricus muscarius*) is amorphous, and soluble in chloroform and ether, but does not dissolve in water. Its solutions show no characteristic absorption bands. It has the composition $C_{19}H_{18}O_6$, and the author calls it provisionally *amanitin*. C. H. B.

**Cardol.** By LEOPOLD SPIEGEL and CARL DOBRIN (*Chem. Centr.*, 1896, i, 112; from *Ber. Pharm. Ges.*, **5**, 309—325).—The composition of different preparations of cardol corresponds with the formula $C_{32}H_{50}O_3$ or $C_{32}H_{52}O_4$; the specimens which give the latter formula, however, lose $H_2O$ when heated, so that the former of the two is the true formula. Cardol does not react with hydroxylamine, but yields a monacetyl derivative, and forms compounds with alkalis. When treated with sodium in boiling amylic alcohol, it is reduced to a brown viscid mass, which has the formula $C_{32}H_{52}O_2$. On distillation with zinc dust, it yields *cardene*, $C_8H_8$, which boils at 122—127°, and is not identical with styrene. Concentrated nitric acid converts cardol into a nitrogenous *substance*, $C_{30}H_{52}NO_{12}$, melting at 105°, the dibasic *cardolic acid*, $C_{15}H_{28}O_7$, which melts at 120°, being also formed. When the insoluble portion of the oxidation product is treated with potassium permanganate, it yields *cardic acid*, $C_{13}H_{24}O_5$, melting at 89°. The direct oxidation of cardol with potassium permanganate yields the monobasic *cardenic acid*, $C_{16}H_{30}O_7$, melting at 126°. The yellow mass formed by the action of nitric acid is reduced by tin and acetic acid to a paraffin-like substance, $C_{15}H_{34}O_2$, melting at 59°.

These results show that cardol is not in any way related to cantharidin, and the authors have found that the cantharidin-like effects of acajou balsam are in reality due to a substance which is soluble in ether, and not to cardol itself. A. H.

**2 : 4 : 1-Dinitrohydroxyquinoline.** By ADOLPH CLAUS and EMIL DEWITZ (*J. pr. Chem.*, 1896, [2], **53**, 532—548).—2 : 4 : 1-*Dinitrohydroxyquinoline*, prepared by nitrating 1-hydroxyquinoline in glacial acetic acid, is a yellow, crystalline powder, decomposes at 276° when heated in a capillary tube, and is insoluble in the usual solvents, but dissolves in hot alkalis and concentrated acids. The *potassium* salt, with $\frac{1}{2}H_2O$, *sodium* salt, with $\frac{1}{2}H_2O$, *ammonium* salt, and *copper* salt, with $1H_2O$, are described, also the double salts, $C_9NH_4(NO_2)_2{\cdot}OK + 2BaCl_2 + 3H_2O$; $C_9NH_4(NO_2)_2{\cdot}OK + 2CaCl_2 + 6H_2O$; $4C_9NH_4(NO_2)_2{\cdot}OK + AgNO_3$(with $\frac{1}{2}H_2O$ ?), and $C_9NH_4(NO_2)_2{\cdot}OK + Pb(NO_3)_2$. Attempts to prepare alkylic ethers from the alkali salts have failed. Salts in which the dinitrohydroxyquinoline has a basic function cannot be isolated, although they appear to exist; the *platinochloride* is of the irregular composition $[C_9NH_4(NO_2)_2{\cdot}OH]_2,2H_2PtCl_6$.

2 : 4 : 1-*Diamidohydroxyquinoline* is obtained by reducing the dinitro-compound with tin and hydrochloric acid; the stannichloride formed must be decomposed by hydrogen sulphide, since alkalis cause a deeply seated change. The *hydrochlorides*, $C_9H_9N_3O,3HCl$ and $C_9H_9N_3O,2HCl$, are brown and red respectively. The free base, isolated by adding excess of sodium carbonate to the solution of the hydrochloride and extracting with chloroform, is a red crystalline powder, soluble in the usual solvents. The *platinochloride*, $C_9H_9N_3O,H_2PtCl_6$, is described. The *diacetyl* derivative,

$$C_9NH_4(NHAc)_2{\cdot}OH,$$

crystallises in yellow needles, and melts and decomposes at 240°; the corresponding *dibenzoyl* derivative melts at 263—264°, and sublimes unchanged.

2 : 4-*Diamidoquinoline* is prepared by heating the diamidohydroxyquinoline hydrochloride with hydriodic acid, iodine, and red phosphorus in a reflux apparatus. The *hydriodide*, $C_9H_9N_3,2HI$, crystallises in red needles, melts at 215—216°, and dissolves in water and alcohol; the *platinochloride*, $C_9H_9N_3,H_2PtCl_6$, is described. The base is identical with that obtained by reducing 2 : 4-dinitroquinoline (this vol., i, 392).

2 : 4 : 1-*Dinitramidoquinoline* is prepared by heating 2 : 4 : 1-dinitrohydroxyquinoline with alcoholic ammonia at 180° for 3—4 hours; it crystallises in yellow needles, melts in a capillary tube at 187—188°, and dissolves in most organic solvents. It is remarkable that this compound has so little basic tendency that it does not even form a platinochloride. By reduction with stannous chloride and hydrochloric acid, it yields 1 : 2 : 4-*triamidoquinoline*, which forms red-brown crystals, and does not melt at 350°; the *hydrochloride*, $C_9H_{10}N_4,3HCl$, is described. A. G. B.

**"Quinine Chlorhydro-sulphate."** By GEORGES (*J. Pharm.*, 1896, **3**, 589—594).—A pharmaceutical preparation of quinine used in France. A careful chemical, microscopical, and polarimetrical investigation has proved it to be a mixture of quinine sulphate and quinine hydrochloride. L. DE K.

**Ketones of the Tropine Group. IV. ψ-Tropigenine.** By RICHARD WILLSTÄTTER (*Ber.*, 1896, **29**, 1636—1639; compare this vol., i, 327, 451, 582).—When nortropinone carbamate is reduced by means of sodium and ethylic alcohol, ψ-tropigenine is produced. The base is obtained as an oil, and is best purified by converting it into the *carbamate;* this is a crystalline powder, which is non-hygroscopic, but dissolves readily in water, and melts at 138—140°, carbonic anhydride being evolved; its solution does not yield precipitates with picric acid or with cold calcium chloride, but the latter, when hot, gives an immediate deposit. The free *base*, $C_7H_{13}NO$, is precipitated in slender needles on adding strong soda to the carbamate; it is readily soluble in water and alcohol, but only sparingly in ether; when exposed to the air, it absorbs aqueous vapour and carbonic anhydride. The *aurochloride*, $C_7H_{13}NO,HAuCl_4$, is obtained as a dense, orange-yellow, crystalline precipitate, soluble in alcohol and in hot water; it crystallises in fern-like leaflets composed of aggregated prisms, and melts and decomposes at 211—212°. The *platinochloride*, $(C_7H_{13}NO)_2,H_2PtCl_6$, crystallises from hot water in anhydrous, shining, red leaflets consisting of aggregations of prisms; it is insoluble in alcohol, and melts and decomposes at about 240°. The *benzoyl* derivative, $C_7H_{12}ONBz$, is more readily soluble in hot water than in cold, and dissolves easily in acetone; it crystallises from water in well defined, highly refractive, rhombic tables, and from alcohol in colourless, shining needles; it melts at 165—166°. The properties of the foregoing compound are very distinct from those of the benzoyl derivative of tropigenin. A. L.

**The Identity of Methylprotocotoïn and Methylhydrocotoïn with the Corresponding Compounds obtained by Ciamician from Leucotin.** By GIOV. B. NEGRI (*Chem. Centr.*, 1896, i, 311—312; from *Rivista di Min. e Crist.*, **13**, 85).—The supposition of Ciamician and Silber (Abstr., 1893, 417), that the leucotin of Jobst and Hesse is a mixture of methylprotocotoïn and methylhydrocotoïn, is confirmed, the author having found that the crystallographic constants are identical with those of the pure compounds. Methylprotocotoïn forms tablets, which are probably monoclinic, and have an angle of extinction of about 26°. Methylhydrocotoïn is also monoclinic, the axial ratio being 1·9913 : 1 : 0·5663, and the angle $\beta = 58° 41'$. A. H.

**Scopolamine and Atroscine.** By OSWALD HESSE (*Ber.*, 1896, **29**, 1776—1785).—The identity of scopolamine and hyoscine has been fully proved by various observers, but Rachlmann states that, physiologically, scopolamine from Scopolia root is superior to hyoscine from hyoscyamus; as this statement is confirmed by others, the latter preparation must contain a new alkaloïd. The author has succeeded in isolating this compound, which he terms *atroscine*, by the fractional crystallisation of anhydrous commercial "scopolamine" hydrobromide from alcohol (97 per cent.), in which the atroscine salt is less soluble. The base, $C_{17}H_{21}O_4N$, is amorphous, melts at about 50°, and is alkaline to litmus paper, but is without effect on phenolphthaleïn. It is isomeric with hyoscine, with which it appears to form a racemic compound. By the action of water at 10°, atroscine forms a hydrate with $2H_2O$, which crystallises in colourless, concentric needles, melting at 36—37°. With potash, it is decomposed, like hyoscine, into oscine and, probably, tropic acid, but the latter is at once converted into atropic acid. The *hydrochloride* crystallises in long, colourless needles, and is optically inactive. No platinochloride could be prepared; the *aurochloride* crystallises in small, yellow plates, melting at 201—202°, and decomposing at 204—206°; at 50°, it dissolves in 690 parts of dilute hydrochloric acid (1 per cent.). The *hydrobromide*, $C_{17}H_{20}O_4N,HBr + \frac{1}{2}H_2O$, crystallises from alcohol in short, rhombic prisms, and from water in large, glassy, rhombic plates; in solubility, it resembles the hyoscine salt, but is optically inactive. The *hydriodide* forms colourless, short, concentric prisms. Attempts to convert atroscine into hyoscine by the action of alkalis, or silver oxide, were unsuccessful; either the alkaloïd decomposed as with potash (see above) or no action took place. The amount of atroscine hydrobromide in commercial hyoscine hydrobromide is readily determined by means of the refractive power; the former compound is inactive, but for the latter, $[\alpha]_D = -22.5°$. Atroscine causes dilation of the pupil to the same extent as atropine, but its general effect on the system is less marked; its action on accommodation both in extent and duration is 2—4 times as great as that of atropine and scopolamine. E. Schmidt has recently suggested that atroscine is identical with *i*-scopolamine, but a comparison of the bases, hydrobromides, and aurochlorides, shows that this is not the case; as *i*-scopolamine is feebly lævogyrate, and the hydrobromide feebly dextrogyrate, *i*-scopolamine is probably a mixture of atroscine and a new dextrogyrate alkaloïd. The author suggests that the name scopolamine should no longer be used.

J. B. T.

**Hyoscine.** By OSWALD HESSE (*Ber.*, 1896, **29**, 1771—1776).—Ladenburg's paper on this subject (Abstr., 1893, i, 739) is first discussed. The author maintains the accuracy of his formula, $C_{17}H_{21}O_4N$, for hyoscine, and Ladenburg's analyses, made with fully purified materials, are in better agreement with the author's than his own formula, $C_{17}H_{23}O_3N$.

When a mixture of tropine and oscine, in hydrochloric acid solution, is treated with platinic chloride, tropine platinochloride is first deposited in small crystals, which have been described by von Lasaulx; if these are allowed to remain in contact with the mother liquor, they disappear, and large, orange-red prisms are formed having the same composition as the former; they appear to be identical with the pseudotropine platinochloride crystals described by Milch. The oscine salt is only deposited when the mother liquor is considerably concentrated. If, in the above experiment, gold chloride is substituted for platinic chloride, oscine aurochloride is deposited first. These facts probably account for Ladenburg's erroneous observations.

Hyoscine forms two very characteristic salts, the aurochloride and hydrobromide. The former crystallises in long, yellow, slightly lustrous plates, melts and decomposes at 198—199°, and at 50° dissolves in 510 parts of dilute hydrochloric acid containing 10 parts of acid (sp. gr. = 1·19) per litre. The hydrobromide is deposited with $3H_2O$ in large, vitreous, rhombic crystals, melting at 100° in their water of crystallisation, $[\alpha]_D = -25·7°$; the anhydrous compound melts at 181°. If the anhydrous salt is recrystallised from alcohol (95 per cent.), colourless, rhombic prisms with $2H_2O$ are formed; from absolute alcohol, anhydrous rhombohedra are obtained. By the action of potash, hyoscine is liberated and quickly decomposed into tropic acid and oscine, the former then slowly changes into atropic acid. It has been previously stated by the author that another alkaloid of lower refractive power is formed under these circumstances, but this is not the case. Sodium, barium and calcium hydroxides act like potash; silver oxide and ammonia liberate hyoscine, which undergoes no further change. J. B. T.

**The Alkaloïds of Anagyris Fœtida.** By ALFRED PARTHEIL and L. SPASSKI (*Chem. Centr.*, 1896, i, 375; from *Apoth. Zeit.*, **10**, 903—904).—The commercial product known as "Anagyrinum hydrobromicum" appears to be a mixture of substances. The seeds of *Anagyris fœtida* contain two alkaloïds, cytisine and anagyrine. The aqueous solution of the latter is lævorotatory, and its *aurochloride* melts at 206—207°. Doubt is cast by the authors on the various formulæ which have been proposed for anagyrine. A. H.

**Synthesis of Cytisine.** By JOH. VAN DE MOER (*Chem. Centr.*, 1896, i, 312; from *Nederl. Tijdschr. Pharm.*, **7**, 362—365).—Cytisine is *apopilocarpine*, and, since pilocarpine belongs to the γ-series, it is probable that cytisine is also a γ-compound. The author is investigating the question experimentally. A. H.

**Gelseminine.** By M. GÖLDNER (*Chem. Centr.*, 1896, i, 111; from *Ber. pharm. Ges.*, **5**, 330—359).—The author has repeated Spiegel's work on gelseminine (Abstr., 1893, i, 492), and confirms his results, so that the statements of Cushny (Abstr., 1893, i, 614) must be considered as erroneous. *Gelseminінemethylammonium hydroxide* melts at 203°. When gelseminine methiodide is distilled with solid potash, four different substances are obtained under varying conditions; a base of the formula $C_{15}H_{24}NO_5$ or $C_{15}H_{22}NO_4$, the *hydrochloride* of which melts at 265°; a *hydrochloride* of the formula $C_{21}H_{29}N_2O_3,HCl$, which melts at 286°; a salt of the composition $C_{10}H_{11}N,HCl$, melting at 303°; and, finally, a resinous substance of the composition $C_{10}H_{13}N$, which is not identical either with tetrahydrotoluquinoline (ortho- or para-) or with tetrahydroisoquinoline. Gelseminine yields a *monacetate* melting at 290°, and a *monobenzoate* melting at 303°. Oxidation with potassium permanganate yields a compound melting at 238°, the empirical formula of which is $C_{18}H_{19}N_2O_9$. A. H.

**Nucleic and Thymic acids.** By ALBRECHT C. L. M. L. KOSSEL and ALBERT NEUMANN (*Zeit. physiol. Chem.*, 1896, **22**, 74—81).—The acid discovered in egg-yolk by Altmann is not nucleïc acid, as the decomposition products of the latter cannot be obtained from that source.

Nucleïc acid is decomposed by hydrolysis into thymic acid, adenine, guanine, and cytosine (compare Abstr., 1894, i, 156). The decomposition is effected in the following manner: 10 grams of nucleic acid is boiled with 500 c c. of water until addition of hydrochloric acid causes no precipitate of unaltered nucleïc acid; the filtered liquid is then made faintly alkaline with baryta water, and allowed to remain one day, when guanine and barium carbonate are precipitated, adenine, cytosine, and barium thymate remaining in solution. The barium thymate is then precipitated by the addition of alcohol, whilst the adenine and cytosine are separated by means of their silver compounds, that of adenine being insoluble in water. The barium thymate is purified by washing, dissolving it in water, and precipitating with alcohol; the addition of barium chloride to the liquid in the latter instance ensures complete precipitation.

*Barium thymate*, $C_{16}H_{23}N_3P_2O_{12}Ba$, contains water of crystallisation, which it slowly loses at 100°; it dissolves readily in water, and, when anhydrous, is excessively hygroscopic. Thymic acid differs from the parent nucleïc acid by its ready solubility in water and dilute mineral acids, the precipitates it yields with albumin or propeptone being also more readily soluble in hydrochloric acid than those afforded by nucleïc acid. Nucleïc acid does not behave as an acid salt of thymic acid, for when it is dissolved in barium hydroxide and the barium salt is precipitated by alcohol, no nucleïn bases can be detected in the liquid, whilst adenine or guanine thymate when subjected to similar treatment at once give evidence of the production of free base. A. L.

**Formation of a Pyridine Derivative from Albumin by boiling with Hydrochloric acid.** By RUDOLPH COHN (*Ber.*, 1896, **29**, 1785—1789).—Caseïn (1 kilo.), when boiled during five hours with concentrated hydrochloric acid (sp. gr. = 1·9, 3 litres), yields tyrosine, leucine, carbonic anhydride, and ammonia in small quantity; aspartic acid, and glutamic acid, in comparatively large quantity a compound which yields iodoform, an oily acid which is still under investigation, and a pyridine derivative, probably $C_5H_7ON$; the latter is separated from the leucine by means of sulphuric acid. It is sparingly soluble in water, crystallises in long, feathery needles, melts at 296°, and readily sublimes; when quickly heated, it decomposes, acid vapours being evolved; it is not changed by alkalis or acids, dilute or concentrated. No salts could be prepared. When distilled with zinc dust in an atmosphere of hydrogen, pyridine is formed. The yield of crude substance is about 0·6 per cent. of the caseïn employed.
J. B. T.

**New Series of Proteïds.** By F. BLUM (*Zeit. physiol. Chem.*, 1896, **22**, 127—131).—If white of egg is diluted with water, and after being filtered from globulins, a little formaldehyde is added to the solution of ovomucoïd and egg albumin, the latter is found to have lost its power of coagulating. The liquid is then distilled until neither the residual liquors nor the distillate give the aldehyde reaction with decolorised magenta; it now has a faintly sweet taste, and an odour of fresh egg-albumin, and when evaporated on the water bath deposits a pellicle of albuminous matter.

The dried albumin is transparent, bright yellow, and readily soluble in water, and in solution of sodium chloride or sulphate. It is precipitated from its solution by mineral acids, absolute alcohol, or acetone; the solution also gives characteristic precipitates with potassium ferrocyanide, tannin, and salts of the heavy metals; violet and red coloration being produced on the addition of alkaline copper solution or mixed acetic and sulphuric acids. When precipitated by acetone, it may be subsequently dissolved by the addition of a few drops of water. It gives the xanthoproteïn and Millon's reactions, and a precipitate of lead sulphide is formed when it is boiled with alkaline lead acetate. Its behaviour is unlike that of any known albumin, and its production by the interaction of formaldehyde may possibly be represented thus,

$$\begin{matrix}-NH_2\\-NH_2\end{matrix} + CH_2O = \begin{matrix}-NH\\-NH\end{matrix}\!\!>CH_2 + H_2O,$$

or,

$$-NH_2 + CH_2O = -N{:}CH_2 + H_2O.$$

A. L.

**Decomposition Products of Proteïds.** By SVEN G. HEDIN (*Zeit. physiol. Chem.*, **22**, 191—196).—As has been shown by Drechsel, albumins, when heated with hydrochloric or phosphomolybdic acid, yield a mixture of bases. From the latter, the author has already isolated arginine, whilst, from the precipitates they yield with silver nitrate, Siegfried has obtained a new base in the form of its hydrochloride, $C_{11}H_{20}N_6O_6,2HCl$ (see Abstr., 1891, 591).

In the present paper, the author describes the results of his investigation of this silver precipitate; the latter is decomposed by hydrogen sulphide, and the aqueous solution of the product is mixed with ammoniacal lead acetate, when a small quantity of a compound containing sulphur is precipitated. The filtrate is then freed from lead, and mixed with ammoniacal silver nitrate, the precipitate formed being decomposed by hydrochloric acid, and the filtered solution evaporated nearly to dryness. The *hydrochloride* of the new base separates in beautiful tables of the composition $C_6H_9N_3O_2,HCl,H_2O$; it is optically inactive, somewhat readily soluble in water, but insoluble in alcohol and ether; its aqueous solution has an acid reaction.

The free *base*, $C_6H_9N_3O_2$, crystallises from water in the form of needles or tables. Its aqueous solution has a feeble alkaline reaction, and does not absorb carbonic anhydride; it gives no precipitate with neutral silver nitrate, but on the addition of ammonia a *silver compound*, $Ag_2C_6H_7N_3O_2,H_2O$, is obtained as a voluminous, amorphous precipitate readily soluble in alcohol.

The above base is possibly identical with that of Siegfried; it appears, also, to be identical with Kossel's histidine, $C_{12}H_{20}N_6O_4$ (see this vol., i, 582), as, although the properties of the hydrochloride, as described by that author, are not in accordance with those of the foregoing salt, the crystals of both have been goniometrically measured, and the results are practically identical. A. L.

**The Behaviour of Caseïn towards Pepsin-hydrochloric acid.** By Ernst L. Salkowski (*Pflüger's Archiv*, 1896, **63**, 401—422).—Several recent writers have shown that caseïn, unlike other nucleo-proteïds, yields a nucleïn which is largely soluble on gastric digestion. The present experiments show that caseïn is wholly soluble in pepsin-hydrochloric acid; the conclusions as to the conditions under which this occurs are the following: complete solution occurs if the presence of dry, hard lumps of caseïn is excluded; this may be done by making a solution of the caseïn before adding the digestive mixture, which should be present in the proportion of 500 to 1 of caseïn. If the proportion is 250 to 1, about 1 per cent. of the caseïn remains undissolved; the residue increases with smaller proportions. The percentage of hydrochloric acid, which is best, is between 0·054 and 0·216; within these limits, difference in amount of digestion does not occur; above the higher limit, digestion is slightly impeded.

W. D. H.

**Phycocyanin, a Crystallisable Proteïd.** By Hans Molisch (*Chem. Centr.*, 1896, i, 111—112; from *Bot. Zeit.*, 1895, i, 131).—The colour of the blue-green algæ or cyanophyceæ is due to chlorophyll, phycoxanthin, and phycocyanin. A solution of the last of these, obtained from *Oscillaria leptotricha* (Kütz), was obtained in crystals by salting out its solution with ammonium sulphate. It has not yet, however, been decided whether the crystals consist of pure phycocyanin. A. H.

**Preparation and Composition of Hæmine Hydrochloride.** By M. Cloetta (*Chem. Centr.*, 1896, i, 260; from *Arch. exp. Path. Pharm.*, **36**, 349—360).—Coagulated blood is freed from serum, washed with sodium sulphate solution, and finally with strong alcohol. The mass is then powdered, dried, and ground up with 96 per cent. alcohol and a few drops of concentrated sulphuric acid; a little alcoholic hydrochloric acid is added to the boiling filtrate, and the whole allowed to cool. Hæmine hydrochloride separates in fascicular groups of long, pointed needles, which have a dark violet colour and a metallic lustre. Alkalis precipitate hæmine as an amorphous, black-brown powder. The recrystallised hydrochloride appears to have the composition $4(C_{30}H_{34}N_3FeO_3,HCl) + C_{30}H_{34}N_3FeO_3$. It seems probable that the specimens analysed by Hoppe-Seyler, who gave to hæmine the formula $C_{34}H_{31}N_4FeO_3 + 2H_2O$, and by Küster and Nencki and Sieber, who arrived at the formula $C_{32}H_{30}N_4FeO_3$, contained xanthine. A. H.

**Phosphocarnic acid.** By Max A. Siegfried (*Zeit. physiol. Chem.*, 1895, **21**, 360—379).—This paper gives full details of the researches on carniferrin, phosphocarnic acid, and carnic acid, short notices of which have been already published (see Abstr., 1895, i, 76 and 313).

A. L.

# Organic Chemistry.

**Preparation of Cyanogen Bromide.** By JOSEPH TCHERNIAC (*Ber.*, 1896, **29**, 2078—2079).—A polemical paper replying to Scholl's criticisms (this vol., i, 585). J. J. S.

**Alcoholic Hydrates.** By H. P. BARENDRECHT (*Zeits. physikal. Chem.*, 1896, **20**, 234—241).—Considering the question of the existence of alcoholic hydrates to be in an unsettled state, the author endeavoured to obtain solid hydrates by cooling alcoholic solutions of various strengths. In the more dilute solutions, well-defined, six-sided crystals were obtained at −40°; these, on analysis, were found to contain 37 per cent. of ethylic alcohol, and hence are not the supposed hydrate, $C_2H_6O,3H_2O$, which should contain 46 per cent. (Abstr., 1894, ii, 374), but are considered by the author to be merely ice crystals. In 75 per cent. alcohol, a second form of crystal was obtained, cubic and isotropic. These crystals are probably also crystals of ice, the dimorphism of which has been previously stated, and this view is supported by the fact that similar crystals are formed in mixtures with other alcohols or with aldehyde. The author concludes, therefore, that no solid hydrates are formed under these conditions, and that the existence of such compounds in solution is very improbable. L. M. J.

**Crotonylic Alcohol and its Ethereal Salts.** By ER. CHARON (*Compt. rend.*, 1896, **123**, 250—252).—In the reduction of crotonaldehyde, the proportion of pinacone formed is unusually high, and amounts to 60 per cent. of the total product. Normal butaldehyde occurs amongst the products, but the corresponding alcohol is not formed, a result which is due to the fact that the zinc-copper couple has no action on saturated aldehydes. It also has no action on crotonylic alcohol. In the reduction of crotonaldehyde by the couple, a small quantity of butaldehyde is formed, but is not further reduced, and a larger quantity (about 25 per cent. of the total product) of the corresponding unsaturated alcohol is produced, and is likewise stable under the conditions of the experiment, the ethylenic grouping remaining unattacked. Paracetaldehyde was found in notable quantity amongst the products, but it most probably pre-existed as an impurity in the crotonaldehyde.

The products of the reduction of crotonaldehyde do not vary appreciably under somewhat wide variations in the dilution of the liquid or in the temperature at which reduction takes place, but a temperature of 0° seems to favour the production of glycol. The process of reduction results in the development of much heat.

The ethereal salts of crotonylic alcohol are readily obtained by the action of the acids or anhydrides, but not by the action of acid chlorides. The *formate* is a crystallisable compound which boils at 112°, sp. gr. = 0·9301 at 0°; the *acetate* boils at 130—131°, sp. gr. = 0·9338 at 0°; the *propionate* boils at 150—151°, sp. gr. = 0·9339 at

0°; the *isobutyrate* boils at 158—159°, sp. gr. = 0·9067 at 0°; the *isovalerate* boils at 178—179°, sp. gr. = 0·9012 at 0°.

The action of acid chlorides on the alcohol yields a somewhat complex mixture containing several isomerides. C. H. B.

**Preparation of Diallylethylic Alcohol.** By ERWIN OBERREIT (*Ber.*, 1896, **29**, 2005—2007).—*Diallylacetamide* is obtained by heating ammonium diallylacetate at 230—260°; it crystallises in long needles, melts at 82·5°, and boils at 265°. *Diallylacetonitrile* is an oil, boiling at 186—188°, and has a pleasant smell and sweet taste. When this is treated in alcoholic solution with sodium, it is converted into *diallylethylamine*, an unpleasant smelling, caustic liquid, which boils at 167°, unites with moisture from the air, has an alkaline reaction, and fumes with hydrochloric acid. The *hydrochloride* is excessively hygroscopic; the *platinochloride* is sparingly soluble. When the hydrochloride is treated with silver nitrite, the stable *nitrite* of the base is formed; at 80°, however, this decomposes, with evolution of nitrogen and production of *diallylethylic alcohol*, which boils at 170—173°, and is not miscible with water. A. H.

**Constitution of Pinacolin.** By MAURICE DELACRE (*Compt. rend.*, 1896, **123**, 245—248).—The author continues the discussion of the constitution of pinacolin (this vol., i, 591; see also Abstr., 1893, i, 244). When pinacolic alcohol is treated with gaseous hydrogen iodide, it yields tetramethylethylene and a small quantity of a liquid which boils below 70—73°, and this, when converted into a bromide and treated with alcoholic potash, seems to yield a small quantity of an acetylenic hydrocarbon. The author considers that the identity of pinacolin with the product obtained by Boutlerow has never been definitely established. The ketone obtained by Boutlerow's method boils at about 105°, and has an odour distinctly different from that of pinacolin, although similar to it. When hydrogenised, it yields an alcohol which boils at 118° but does not solidify in a mixture of sodium sulphate and hydrochloric acid, and is therefore not identical with pinacolic alcohol. When heated with hydrogen iodide, this alcohol yields tetramethylethylene; its other properties remain to be investigated.

When Boutlerow's ketone is treated with 3½ times its weight of concentrated hydrobromic acid, heat is developed, and the two liquids mix perfectly, but the mixture remains limpid and retains its pale straw colour for many hours. Pinacolin under the same conditions becomes almost black, and very soon forms an abundant precipitate. C. H. B.

**Action of Sulphur Chloride on Penterythritol.** By J. BOUGAULT (*Compt. rend.*, 1896, **123**, 187—189).—When penterythritol (Abstr., 1892, 127) is boiled with five times its weight of sulphur chloride until evolution of hydrogen chloride ceases, it yields a mixture of *penterythritol bisulphite*, $C_5H_8(SO_3)_2$, and *penterythritol dichlorhydrin*, $C_5H_8Cl_2(OH)_2$. The bisulphite crystallises from boiling alcohol in bulky, rhomboidal lamellæ, which melt at 153—154°, and sublime without decomposing. It is almost insoluble in water, and only slightly soluble in common organic solvents at the ordinary temperature, but dissolves somewhat readily at their boiling points. It has a neutral reaction, and does not change when boiled with water, but in presence of a trace of acid it is partially decomposed. When boiled with aqueous potash, it is completely converted into potassium sulphite and penterythritol. Dry hydrogen chloride has no action on the compound at its melting point.

Penterythritol dichlorhydrin can be crystallised from ether or benzene, and forms monoclinic crystals, $a : b : c = 0.8210 : 1 : 0.6338$, and $\beta = 84° 4'$. It melts at 65°, and boils at 150—155° under reduced pressure. It is soluble in water, very soluble in alcohol and ether, less soluble in benzene and chloroform, insoluble in carbon bisulphide. When boiled with aqueous potash, it is completely converted into penterythritol.

The bisulphite is not affected by boiling sulphur chloride, and hence it would seem that the formation of the two compounds is simultaneous, and is probably represented by the equation

$$C_5H_8(OH)_4 + 4S_2Cl_2 = S_6 + 6HCl + C_5H_8Cl_2(OH)_2 + C_5H_8(SO_3)_2.$$

C. H. B.

**Mixed Aliphatic Secondary Amines.** By RICHARD STOERMER and VICTOR VON LEPEL (*Ber.*, 1896, **29**, 2110—2121; compare this vol., i, 275 and 298).—*Methylpropylamine* is a colourless liquid of ammoniacal, fish-like odour, has a sp. gr. = 0·7204 at 17°, and boils at 62—64°; it is very hygroscopic, and, being very volatile at ordinary temperatures, burns with a luminous flame when ignited. It is prepared from methylpropylaniline, which is converted into the nitroso-derivative, and the hydrochloride heated with a 10 per cent. solution of soda, the base being collected in concentrated hydrochloric acid, which is then evaporated to dryness and treated in the same way. The *hydrochloride* crystallises in white, deliquescent scales; the *platinochloride* in red needles, which decompose and melt at 200°; the *aurochloride*, which is readily reduced, crystallises in long, yellow needles. The *carbamide* and *phenylcarbamide* melt at 95° and 89° respectively, whilst the *phenylthiocarbamide* is a yellowish oil, which does not solidify at low temperatures; the *nitroso*-derivative is a deep yellow liquid, which boils at 175—176°, and *methylpropylamine methylpropyldithiocarbamate* is a viscous, yellowish oil.

*Methylisobutylamine* is a limpid, colourless liquid of ammoniacal, fish-like odour, and is highly inflammable; it has the sp. gr. = 0·7222 at 18°, and boils at 76—78°. It is formed from the *base*, $CHPr^{\beta}:NMe$, a colourless liquid, boiling at 65—70°, produced by the action of methylamine on isobutaldehyde, and is obtained from it by reduction with sodium and alcohol. The *hydrochloride*, which is but slightly hygroscopic, crystallises in white leaflets, and melts at 177—179°; the *platinochloride* forms deep red prisms, and melts at 192°. The *carbamide* and *phenylcarbamide* melt at 145—146°, and 124—125° respectively, and the *phenylthiocarbamide* crystallises from dilute alcohol in white leaflets, and melts at 92°; the *nitroso*-derivative boils at 186—188°, and *methylisobutylamine methylisobutyldithiocarbamate* crystallises in yellow needles, and melts at 52°. The *benzoyl* derivative is a colourless oil of aromatic odour, and boils at 290—292°.

*Methylisoamylamine* is obtained when isovaleraldehyde is employed instead of isobutaldehyde, and is a colourless, limpid liquid, of highly disagreeable, fish-like odour; it has the sp. gr. = 0·7390 at 22°, and boils at 108°. The *hydrochloride* is not hygroscopic, and melts at 177°; the *platinochloride* crystallises in small, yellow needles, and melts at 196°. The *carbamide* and *phenylcarbamide* melt at 122° and 100° respectively, and the *phenylthiocarbamide* at 43°; the *nitroso*-derivative and *benzoyl* derivative boil at 206° and 296—298° respectively, and *methylisoamylamine methylisoamyldithiocarbamate* is a yellowish oil.

The *carbamide* of methylisobutylhydrazine, $NH_2\cdot CO\cdot NH\cdot NMe\cdot C_4H_9$, crystallises in white needles, and melts at 99°. M. O. F.

**Electrolysis of Acids of the Acetic Series.** By JULES HAMONET (*Compt. rend.*, 1896, **123**, 252—254).—The author finds that, contrary to the statements of Kolbe, in many cases when solutions of acids of the acetic series are electrolysed, scarcely any paraffin is produced, but an olefine is the chief product; and also that an alcohol containing $C_n$ is always formed from an acid containing $C_{n+1}$. The alcohol seems to result from the hydrolysis of the ether that is well known to be formed, or else from the hydration of the olefine. More condensed products are also always produced in small quantity.

With a current of 5 ampères and 6 volts, potassium butyrate yields propylene, a small quantity of isopropylic alcohol, and a still smaller quantity of isopropylic butyrate; neither hexane nor primary propylic alcohol is formed. Potassium isobutyrate, under the same conditions, yields practically the same products. C. H. B.

**Development of Rancidity in Fats.** By EDUARD SPAETH (*Zeits. anal. Chem.*, 1896, **35**, 471—493).—Although the most divergent views have been put forward with regard to the cause of the development of rancidity in fats, the more recent researches (those of Duclaux, Ritsert, and von Klecki) have demonstrated conclusively that the process is one of oxidation by the oxygen of the air, and that it is favoured by access of light. By the examination of 14 samples of lard which had been kept for three years in loosely corked flasks, the author has endeavoured to elucidate more in detail the changes which have taken place.

Concurrently with the development of free acidity, a marked decrease in the capacity for absorbing iodine takes place. Of the free acids produced, the greater part is insoluble in water, but soluble acids, and others which are volatile (by the Reichert-Meissl process) are also produced. Amongst the soluble acids, formic, acetic, and butyric have been detected with certainty. The average molecular weight of the total fatty acids is lowered. The iodine absorption of the fluid fatty acids (Muter and De Koningh's number) falls to about the same extent as that of the fat itself. The free acids of the rancid fat exhibit the same iodine absorption as the neutral fat. The refractive index of the fat shows an increase; that of the fatty acids does not. An increase in the acetyl-number (Abstr., 1887, 620) of the fat occurs, and generally a slight rise in the melting point takes place.

The conclusions drawn from these facts are as follows. In the first place, the glycerides, both of the saturated and unsaturated fatty acids, split up into glycerol and the free acids. The unsaturated acids (mainly oleic) then further decompose into acids containing fewer carbon atoms, together with (as shown by von Raumer) aldehydes; hydroxy-fatty acids are at the same time formed. Simultaneously, the unsaturated acids undergo polymerisation, but the polymerides split up again into the simpler acids when saponified.

M. J. S.

**Dehydroundecylenic acid, $CH⋮C\cdot[CH_2]_8\cdot COOH$.** By Friedrich Krafft (*Ber.*, 1896, **29**, 2232—2240).—Experiments are described tending to prove the correctness of the formula

$$CH_2:CH\cdot[CH_2]_8\cdot COOH$$

for undecylenic acid.

On treating undecylenic acid dibromide with alcoholic potash at high temperatures, a rearrangement of the atoms evidently ensues, with the formation of undecolic acid, $CMe⋮C\cdot[CH_2]_7\cdot COOH$, the correctness of the formula for which is placed beyond doubt from its ready conversion into azelaic acid, $COOH\cdot[CH_2]_7\cdot COOH$, on oxidation. The rearrangement is similar to that which occurs in the production of hexadecylidene from tetradecylacetylene by the same method.

That not only the temperature, but also the alcoholic potash, plays an important part in this rearrangement, is shown by the treatment of bromundecylenic acid in alcoholic solution with potassium carbonate, and the subsequent dry distillation of the potassium salt thus formed; by these means, a compound quite different from undecolic acid, although isomeric with it, is produced. This new acid, for which the name *dehydro-undecylenic acid* is proposed, melts at 42·5—43°, and yields sebacic acid on oxidation, which is readily distinguished from the azelaic acid produced on the oxidation of undecolic acid. It appears then, that under these circumstances, undecylenic acid has been converted, without rearrangement, into dehydro-undecylenic acid, $CH⋮C\cdot[CH_2]_8\cdot COOH$.

By heating dehydro-undecylenic acid with a very concentrated aqueous solution of potash at 180°, it is completely converted into undecolic acid (m. p. 58°).

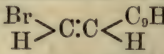
The close relation of dehydro-undecylenic acid to undecylenic acid is further shown from its direct production from the dibromide of undecylenic acid on treatment with alcoholic potash at low temperatures.

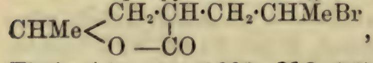
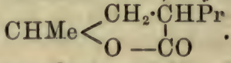
In the same way, monobromhexadecylene, when treated with alcoholic potash at low temperatures, yields tetradecylacetylene,

$$C_{14}H_{29}\cdot C⋮CH,$$

whilst, as has been previously shown, at higher temperatures, rearrangement ensues, with the formation of methyltridecylacetylene, $C_{13}H_{27}\cdot C{:}CMe$.

*Ethylic dehydro-undecylenate*, $CH{:}C\cdot[CH_2]_8\cdot COOEt$, is formed on heating the acid with dry potassium carbonate, and warming the potassium salt thus formed with ethylic iodide; it is a colourless oil boiling at 145° (15 mm.), and behaves as a true acetylene derivative, forming a silver compound crystallising in glistening plates, from which, on treatment with hydrochloric acid, the ethylic salt is regenerated.

In the production of dehydro-undecylenic acid from bromundecylenic acid, it was noticed that a comparatively large quantity of the bromo-acid remained unchanged; this was separated and again subjected to treatment with alcoholic potash, remaining, however, unaltered. Only after prolonged heating in an autoclave at 180° with alcoholic potash was undecolic acid produced, without the intermediate formation of dehydro-undecylenic acid. The author explains this fact by supposing that two isomeric modifications of bromundecylenic acid exist, the *trans*-configuration  $\substack{Br\\H}{>}C{:}C{<}\substack{C_9H_{17}O_2\\H}$ being comparatively stable towards alcoholic potash. A similar instance was noted in the case of hexadecylene bromide. J. F. T.

**The Combination of Hydrogen Bromide with Diallylacetic acid and Diallylacetone.** By Erwin Oberreit (*Ber.*, 1896, **29**, 1998—2005).—When hydrogen bromide is passed into an alcoholic solution of ethylic diallylacetate, the crude product contains ethylic dibromodipropylacetate, together with the bromopropylvalerolactone,  $CHMe{<}\substack{CH_2\cdot CH\cdot CH_2\cdot CHMeBr\\ O\ —\ CO}$, previously obtained by Hjelt and Fittig (*Annalen*, 1882, **216**, 73) by the action of hydrogen bromide on the free acid. This is shown by the fact that when the crude product is treated with alcohol and zinc dust, it yields dipropylacetic acid and *α-propylvalerolactone*,  $CHMe{<}\substack{CH_2\cdot CHPr\\ O\ —\ CO}$. The latter is an oil which boils at 228—231°, has a characteristic odour, and is almost insoluble in water. The *silver salt* of the corresponding acid crystallises in small needles. The *methylic salt* is a thick oil, and decomposes into the lactone and methylic alcohol when heated or simply kept over sulphuric acid.

When diallylacetone is treated in ethereal solution with sodium, it is converted into asymmetric *diallylisopropylic alcohol*, which is an oil boiling at 184—185°. This alcohol readily unites with hydrogen bromide, forming dibromodipropylisopropylic alcohol,

$$CH(CH_2\cdot CHMeBr)_2\cdot CHMe\cdot OH.$$

When treated with alcohol and zinc dust, this product is converted into a substance boiling at 158—159°, which appears to have the formula $C_8H_{16}O_4$, but the constitution of which is not yet understood, and a *hydrocarbon*, $C_9H_{20}$, which boils at 138—139°; it has the sp. gr. 0·7407, and the molecular refraction 43·4. A. H.

**$\alpha\beta$-Dimethylglutaric acid.** By CLEMENS MONTEMARTINI (*Ber.*, 1896, **29**, 2058—2061).—The author has shown (*Real. Accad. Lincei*, **4**, 110) that by the interaction of ethylic sodiomethylmalonate and alkylic salts of $\gamma$-chlorobutyric acid, two acids are obtained, one, a solid, identical with $\alpha$-methyladipic acid, and the other, a liquid, of uncertain structure. The two foregoing acids are not interconvertible, and are therefore not stereoisomeric; it appeared probable, therefore, that the production of the liquid acid was due to the initial formation of a crotonic acid whose condensation with ethylic sodiomethylmalonate would result in the production of $\alpha\beta$-dimethylglutaric acid. The latter substance was therefore synthesised in the following manner.

Twenty grams of ethylic methyllevulinate were mixed with 8·3 grams of potassium cyanide, and the whole gradually added to 24 grams of ice-cold sulphuric acid. After remaining 24 hours, the liquid was diluted, and the precipitated oil separated and hydrolysed with alcohol and hydrogen chloride. The excess of alcohol was then distilled off, and the product shaken with water and extracted with ether, when 14 grams of an oil, consisting of ethylic $\alpha$-hydroxy-$\alpha\beta$-dimethylglutarate, was obtained. This was at once heated with hydriodic acid during six hours, and the whole once more extracted with ether. In this way an oily mixture of acids was obtained, from which crystals of glutaric acids separated; the liquid portion was distilled under reduced pressure, when it passed over at about 200°, undergoing partial conversion into the anhydride. The pure acid finally obtained gave numbers agreeing with those required for a dimethylglutaric acid, and consisted of a non-crystallisable liquid. It yielded a crystalline calcium salt, from which the silver salt was obtained as a grey-white, crystalline substance, somewhat soluble in boiling water. When treated with acetic chloride, it gives the anhydride; the anilic acid and anilide are readily obtained in the form of oils.

The synthetical $\alpha\beta$-dimethylglutaric acid is identical in every respect with the liquid acid obtained from alkylic $\gamma$-chlorobutyrates and ethylic sodiomethylmalonate. A. L.

**Lyxonic acid.** By EMIL FISCHER and OTTO BROMBERG (*Ber.*, 1896, **29**, 2068; compare this vol., i, 348).—The authors confirm Bertrand's statement (*Bull. Soc. Chim.*, 1896, [3], **15**, 592) that the phenylhydrazide of lyxonic acid crystallises with $2H_2O$.

J. J. S.

**Derivatives of Formylcarbamide.** By TH. VON GORSKI (*Ber.*, 1896, **29**, 2046—2050).—Formylcarbamide melts at 168—169°, and not, as has been stated, at 159°; it crystallises from acetic acid and alcohol, and, when its aqueous solution is evaporated over sulphuric acid, decomposes into formic acid and carbamide.

*Formylmalonuric acid*, $CHO\cdot NH\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot COOH$, is formed when formylcarbamide and malonic acid, in molecular proportion, are dissolved in glacial acetic acid and gently warmed on the water bath. The whole sets to a crystalline pulp, which, after filtration and extraction with ether, is crystallised from hot water or acetic acid. It forms a white, silvery mass of crystals, and melts at 189—199°, the fusion being accompanied by frothing; it is sparingly soluble in hot water, acetic acid, and alcohol. When it is boiled with alkalis, and the resulting solution acidified and distilled, formic acid is found in the distillate. The *barium* salt, $(C_5H_5N_2O_5)_2Ba$, is precipitated, on the addition of barium chloride to an ammoniacal solution of the acid. The *silver* salt, $C_5H_5N_2O_5Ag$, is obtained as a white, crystalline precipitate, rapidly affected by light; it dissolves somewhat readily in water, but is only sparingly soluble in alcohol.

*Formylsuccinuric acid*, $CHO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}C_2H_4{\cdot}COOH$, melts at 136—138°, dissolves sparingly in water and alcohol when cold, but readily when hot. The *silver* salt, $C_6H_7N_2O_5Ag$, is crystalline, and dissolves very readily in water. The *methylic* salt crystallises in white needles, and melts at 63—65°.

*Formyloxaluric acid*, $CHO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}COOH + 3H_2O$, is readily soluble in cold water, but with difficulty in boiling alcohol; from either solvent it separates in beautiful needles, and melts and gives off gases at 175°. The *barium* salt, $C_4H_2N_2O_5Ba$, is somewhat soluble in water, and, as it contains two equivalent proportions of barium, it is probable that an imidic hydrogen is here replaced. The *silver* salt, $C_4H_3N_2O_5Ag$, is crystalline and white. Formyloxaluric acid, when dried at 115—120°, slowly evolves carbonic oxide, and yields cyanuric acid.

On attempting to prepare formylmaluric acid from malic acid, in the above manner, the *ammonium* salt, with $H_2O$, is produced; this crystallises from water in shining, transparent leaflets melting at 128—130°; its aqueous solution, on admixture with silver nitrate, yields a precipitate of the *silver* salt, $C_6H_7N_2O_6Ag$. The latter is readily decomposed by hydrogen sulphide, with production of free *formylmaluric* acid, $HCO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, a thick oil excessively soluble in water.

*Formylracemuric acid*,

$$HCO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH + H_2O,$$

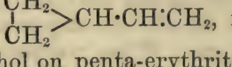
crystallises in elongated tables; its water of crystallisation is, in part, retained at 120°, but, at 256°, the substance melts and decomposes; it is soluble in cold water and alcohol, but insoluble in ether. A. L.

**Alloxantin as a Decomposition Product of Convicin from Sow-beans and Vetches.** By C. HEINRICH L. RITTHAUSEN (*Ber.*, 1896, **29**, 2106—2107; compare this vol., i, 416).—By further tests, the author has fully established the identity of alloxantin from convicin with alloxantin from uric acid. M. O. F.

**Formation of Active β-Asparagine.** By ARNALDO PIUTTI (*Ber.*, 1896, **29**, 2069—2071).—Alcoholic ammonia reacts with lævorotatory bromosuccinamic acid at the ordinary temperature to form ammonium fumarate, which decomposes at 210—212°. When, however, the bromosuccinamic acid is heated with excess of alcoholic ammonia at 160°, a small quantity of aspartamide (Abstr., 1887, 1031) is formed. Aspartamide, when heated with aqueous ammonia at 100—105°, yields an inactive asparagine which, according to the crystallographic researches of La Valle, consists of a mixture of equal parts of the two optically active asparagines. The method is not to be recommended, either for simplicity or good yield.

By the action of a concentrated alcoholic solution of ammonia on maleïc anhydride at 105—110°, a yellow substance is obtained; this, when dissolved in water and treated with Peligot's copper oxide, gradually yields small crystals of an insoluble copper salt.

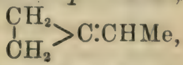
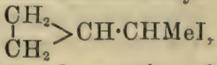
This copper salt, when treated with hydrogen sulphide, yields a mixture of the two natural asparagines. About a fourth of the anhydride is converted by this method into $\beta$-asparagine, and the author recommends the method as a convenient one for the preparation of *d*-asparagine. J. J. S.

**Vinyltrimethylene.** By Gabriel Gustavson (*J. pr. Chem.*, 1896, [2], **54**, 97—104).—*Vinyltrimethylene*,  $\begin{array}{l}CH_2\\ \mid\\ CH_2\end{array}\!>CH{\cdot}CH{:}CH_2$, is a product of the action of zinc dust and alcohol on penta-erythritol tetrabromhydrin (Abstr., 1892, 127). Equal weights of zinc dust and the tetrabromhydrin are mixed in a flask and covered with aqueous alcohol (40—60 per cent.); the flask is provided with a vertical tube to condense as much of the alcohol as possible, and the other end of the tube opens into a receiver cooled by ice-cold water. The flask is warmed on the water bath until the action begins, and again when it has abated, so as to distil over the hydrocarbon. The distillate is washed with water and dried by calcium chloride; the yield is 70—75 per cent. of the weight of the penta-erythritol.

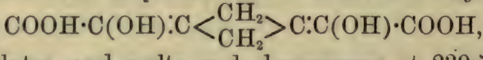
Vinyltrimethylene boils at 40°; its specific gravity is 0·7237 at 18°/4°, 0·7431 at 0°/4°, and 0·7229 at 20°/0°; its odour resembles that of allyl compounds, but is somewhat sweeter. It combines with two atoms of bromine, the *bromide*, $C_3H_5{\cdot}CHBr{\cdot}CH_2Br$, boiling at 185—190°, at which temperature slight decomposition occurs.

Oxidation of the hydrocarbon with permanganate yields the *glycol*, $C_5H_8(OH)_2$, even when sufficient available oxygen is present to form the compound $C_5H_8(OH)_4$. The glycol is a syrupy liquid of sweet taste; it boils at 206—207°, does not solidify at $-20°$, and has a sp. gr. $= 1{\cdot}094$ at 0°/0° and 1·059 at 20°/0°; it is readily brominated to the dibromide, and oxidised by nitric acid to $\alpha\gamma$-hydroxyglutaric acid.

The refractive index of the hydrocarbon, calculated according to the formula $\frac{M}{d}\left(\frac{n^2-1}{n^2-2}\right)$, is, for sodium light, $\mathfrak{M} = 23{\cdot}40$ at 18·5°, and 23·39 at 20°. The value, calculated according to Brühl's method, is 22·6. A. G. B.

**Ethylidenetrimethylene.** By Gabriel Gustavson (*J. pr. Chem.*, 1896, [2], **54**, 104—107).—*Ethylidenetrimethylene*,  $\begin{array}{l}CH_2\\ \mid\\ CH_2\end{array}\!>C{:}CHMe$, is prepared from the product of the action of hydriodic acid on vinyltrimethylene (preceding abstract). This *iodide*,  $\begin{array}{l}CH_2\\ \mid\\ CH_2\end{array}\!>CH{\cdot}CHMeI$, is obtained by adding rather less than the calculated quantity of vinyltrimethylene to a saturated (at 0°) solution of hydrogen iodide in glacial acetic acid; after 12 hours, the solution is poured into water, and the separated iodide is washed with sodium hydrogen sulphite solution. The iodide boils at 57° (50 mm.); its sp. gr. = 1·625 at 0°/0°, and 1·598 at 20°/0°. By Meyer and Locher's test, it gives a green colour to the chloroform.

The new hydrocarbon is obtained by heating the iodide in a sealed tube at 100°, with alcoholic potash, for 10 hours, and then adding water to the contents of the tube to separate the hydrocarbon. It boils at 37·5° (750 mm.), and differs in odour from vinyltrimethylene. Its sp. gr. = 0·7235 at 0°/4°, and 0·7052 at 18°/4°; its refraction is $\mathfrak{M} = 23·5$. In chemical behaviour, ethylidenetrimethylene closely resembles vinyltrimethylene. The *iodide*, obtained by the action of hydrogen iodide on the hydrocarbon, boils at 54° (35 mm.), and is somewhat lighter than the above iodide, sp. gr. = 1·588 at 0°/0°, and 1·559 at 20°/0°; by Meyer and Locher's test it gives no colour to the chloroform. When warmed with water, the iodide yields an alcohol which boils at 114—117°, and is being investigated. A. G. B.

**Tetramethylene-1 : 3-dioxalylic acid.** By O. KALTWASSER (*Ber.*, 1896, **29**, 2273—2281).—Paraformaldehyde reacts with pyruvic acid in presence of sulphuric acid to form *tetramethylene*-1 : 3-*dioxalylic acid*,  $COOH·C(OH)\!:\!C{<}^{CH_2}_{CH_2}{>}C\!:\!C(OH)·COOH$, which crystallises in plates, and melts and decomposes at 239·5—240·5°. The aqueous solution of the acid gives a deep reddish-brown coloration with ferric chloride, and reduces ammoniacal silver solution and Fehling's solution. The acid is very readily decomposed by alkalis, with formation of oxalic acid and ethylene.

The *potassium* salt crystallises in matted needles, and the *silver salt* in lustrous plates. The *piperidine salt* also forms plates, and melts at 145—147°. The *phenylhydrazine salt* is deposited from an alcoholic solution of the two constituents in groups of concentrically arranged needles, which melt at 194°.

In acetic acid solution, however, phenylhydrazine yields the *phenylhydrazide* of the acid, which is a yellow, crystalline, sparingly soluble substance, decomposing and melting at 225—227°.

Concentrated sulphuric acid converts the acid into an *anhydride*, $C_8H_4O_4$, which crystallises in prisms, and melts above 300°. Alkalis convert it first into the acid, and then into the decomposition products of the latter. The acid readily combines with 4 atoms of chlorine or bromine. The *chlorine additive product* crystallises in white needles melting and decomposing at 182·5°—183·5°, whilst the *bromine compound* melts and decomposes at 165—170°. The molecular weight of the acid in alcoholic solution corresponds with the formula given above, and its properties show that it has the constitution represented by this, and not by the tautomeric, formula. The paraformaldehyde, therefore, in the formation of this acid reacts as methylene glycol. The acid is accompanied by a second acid melting at 284·5—286·5°, the constitution of which has not yet been determined. A. H.

**Pentamethenylmalonic acid and Pentamethenylacetic acid.** By AART VERWEY (*Ber.*, 1896, **29**, 1996—1998).—Iodopentamethylene reacts with ethylic sodiomalonate, in presence of toluene, to form *ethylic pentamethenylmalonate* [*cyclopentylmalonate*],

$$\begin{matrix} CH_2{\cdot}CH_2 \\ | \\ CH_2{\cdot}CH_2 \end{matrix}\!\!>CH{\cdot}CH(COOEt)_2,$$

which boils at 137—138° (pressure = 13 mm.). It is very readily hydrolysed by alcoholic potash, and the *potassium salt* is a hygroscopic, crystalline powder. The *free acid* crystallises in slender, white needles, which melt at 162—163°, and are readily soluble in water, alcohol, and ether. It decomposes when heated, forming *pentamethenylacetic* [*cyclopentylacetic*] *acid*, $C_5H_9{\cdot}CH_2{\cdot}COOH$, which is an oil boiling at 139—140° (pressure = 26 mm.). The *silver salt* crystallises from hot water in slender needles. The *ethylic salt* boils at 191—192°. A. H.

**Influence of Substitution on the Course of some Reactions.** By PAVEL IW. PETRENKO-KRITSCHENKO and E. ARZIBASCHEFF (*Ber.*, 1896, **29**, 2051—2054).—When hexamethylene ketone and benzaldehyde react in presence of sodium ethoxide, a condensation product, *dibenzylidenehexamethylene ketone*, $CH_2<\begin{matrix} CH_2{\cdot}C(CHPh) \\ CH_2{\cdot}C(CHPh) \end{matrix}>CO$, is obtained; this separates from alcohol, in which it is sparingly soluble, in yellow crystals, and melts at 117°.

Ethylic dimethyl- and diethyl-acetonedicarboxylates do not readily react with aldehydes under normal conditions, benzaldehyde yielding little or no condensation product; acetaldehyde, however, when treated with the above salts in presence of hydrogen chloride, yields some quantity of a substance of high-boiling point, the description of whose properties the authors defer.

That the difference in the behaviour of acetaldehyde and of benzaldehyde under the foregoing conditions is not due to the greater molecular weight of the latter is shown by the ready interaction of isobutylic acetonedicarboxylate (whose molecular weight is equal to that of ethylic diethylacetonedicarboxylate) and benzaldehyde. *Isobutylic acetonedicarboxylate*, prepared by saturating a mixture of the constituents with hydrogen chloride, boils at 220° under 120 mm. pressure; it reacts readily, both with benzaldehyde and with acetaldehyde, yielding, in the latter instance, a thick, oily *product*, which boils at 218—223° under 60 mm. pressure, and probably has the constitution $O<\begin{matrix} CHMe{\cdot}CH(COO{\cdot}C_4H_9) \\ CHMe{\cdot}CH(COO{\cdot}C_4H_9) \end{matrix}>CO$.

The authors are of opinion that the above facts are to be explained on stereochemical considerations. A. L.

**"Excited" Metals (Metal Couples). Use of Excited Aluminium for Reduction in Neutral Solution.** By HANS WISLICENUS (*J. pr. Chem.*, 1896, [2], **54**, 18—65).—The author deems it better to speak of a metal the activity of which is enhanced by contact with another metal as "excited" (*activirte*), than to adopt the name "metal couple," suggested by Gladstone and Tribe. Some details of the application of aluminium excited by contact with mercury are given, the principles of which have already received notice (Abstr., 1895, i, 437, 634). The best method of preparing aluminium in this condition consists in covering aluminium powder ("aluminiumgries") with a solution of mercuric chloride in absolute alcohol, made by diluting a saturated solution with 10 times its volume of the solvent; after a few seconds, the powder is washed with absolute alcohol and ether. In the event of alcohol being objectionable, ether may be substituted as the solvent for the mercuric chloride.

It is especially for reduction in neutral solutions that excited aluminium is applicable. Its action on an aqueous alcoholic solution of nitrobenzene produces aniline, unless the temperature be kept at 40—50°, when $\beta$-phenylhydroxylamine is formed. A better yield (85—90 per cent. of that theoretically possible) of the latter is obtained when an ethereal solution of nitrobenzene is used; cooling is here essential. Orthonitracetophenone reacts with the aluminium more easily than nitrobenzene does; the product appears to be a hydroxylamine derivative, but has not yet been identified.

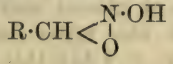
The conversion of ethylic oxalacetate into ethylic malate by excited aluminium is attended by a much better yield than when sodium amalgam is used. The reduction of ketones by this method avoids the formation of the resinous products which characterise other methods; the behaviour of several ketones under this treatment is described. The discussion between Friedländer, Debus, and Eghis concerning the reduction of ethylic oxalate by sodium amalgam, renders the behaviour of this compound under the new method in neutral solution of especial interest; the chief products prove to be ethylic glycollate and alcohol, a little ethylic desoxalate being formed at the same time. Reduction of the azo-group to the hydrazo-group is particularly smoothly effected by excited aluminium.

A. G. B.

**Isomerism of Nitro-compounds. II.** By ARTHUR R. HANTZSCH and OTTO W. SCHULTZE (*Ber.*, 1896, **29**, 2251—2267; compare this vol., i, 353).—Isophenylnitromethane, when rapidly heated, melts at 84°, and not at 74—76°, as previously stated. The copper salt, $(CHPhNO{\cdot}O)_2Cu$, crystallises in silky needles. When reduced with sodium amalgam, the isonitro-compound yields benzsynaldoxime. All isonitro-compounds and their salts give a sky-blue coloration when they are suspended in ether and treated with a current of hydrogen chloride, or with acetic chloride.

*Parabromobenzylic iodide* is obtained by boiling the bromide with potassium iodide solution; it melts at 80—81°, and reacts with silver nitrite to form *parabromophenylnitromethane.* When the sodium salt of this compound is decomposed in aqueous solution by carbonic anhydride, the *normal compound* (*parabromo-ω-nitrotoluene*) is precipitated; this crystallises in large, lustrous prisms, melts at 60°, and gives no coloration with ferric chloride. 100 grams of water at 0° dissolve 0·008 gram of it. The isomeric *isobromophenylnitromethane* is precipitated when hydrochloric acid is added to a solution of the sodium salt. It crystallises in needles, melts at 89—90°, and yields a brownish-red coloration with ferric chloride. 100 grams of water at 0° dissolve 0·056 gram of this substance. When kept, either alone or in solution, it passes into the normal compound. Since the latter does not give the ferric chloride reaction, the passage of the iso-compound into the normal form in solution can be readily followed. Water assists the change in this direction to the greatest extent, chloroform to the least.

That the iso-compound passes into the normal compound in aqueous solution is shown by the fact that the conductivity of an acidified solution of the sodium salt very rapidly decreases for some time, and then becomes constant. This is due to the fact that the free isonitro-compound acts as an acid, and conducts rather better than acetic acid, whilst the normal compound acts as a non-electrolyte. This change of the iso- into the normal-compound in aqueous solution appears to be usually accompanied by the formation of a small amount of nitrous acid. The normal compound cannot iself form salts, but is at once converted by alkalis into the iso-compound, which then dissolves. The normal compounds do not react with phenylic isocyanate, whereas the iso-compounds form diphenylcarbamide. It is found, by the cryoscopic method, that when the iso-compound is dissolved in benzene, its molecular weight is at first twice that of the normal compound, but that it rapidly decreases until it has reached half of its former value. On the other hand, the salts appear to have the monomolecular formulæ.

The authors ascribe the formula $R{\cdot}CH_2{\cdot}NO_2$ to the normal compounds, and  $R{\cdot}CH<\begin{matrix}N{\cdot}OH\\ |\\ O\end{matrix}$ to the iso-derivatives. A. H.

**Nitration of Saturated Hydrocarbons. II.** By MICHAEL I. KONOWALOFF (*Ber.*, 1896, **29**, 2199—2205; compare Abstr., 1894, i, 265, 277, and 1895, i, 633). I. [With NIKITIN].—Diisoamyl, on treatment with dilute nitric acid, yields a tertiary nitro-derivative together with a small quantity of a mixture of two secondary nitro-compounds, namely, $CHMe_2{\cdot}CH(NO_2){\cdot}[CH_2]_3{\cdot}CHMe_2$ and

$$CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NO_2){\cdot}[CH_2]_2{\cdot}CHMe_2.$$

This mixture, on distillation under a pressure of 25 mm., can be separated into a larger fraction which passes over at 129—132° and a smaller fraction which boils at 132—135°; the former fraction does not crystallise when placed in a freezing mixture, and has a sp. gr. = 0·9115 at 20°/0°. The mixture of secondary nitro-compounds, on reduction, yields a mixture of *amines*, from which a *decylamine*, $C_{10}H_{21}{\cdot}NH_2$ was obtained, boiling at 190—192°, and having a sp. gr. = 0·7934 at 20°/0°. Its *hydrochloride*, *nitrate*, and *aurochloride* do not crystallise readily, but the *platinochloride*, which is only sparingly soluble in water, but readily in alcohol, is characteristic. Another product of the reduction of the secondary nitro-compounds is a neutral ketonic substance which gives no crystalline compound with sodium hydrogen sulphite.

A *dinitro*-derivative, $C_{10}H_{20}(NO_2)_2$, was also obtained by the action of dilute nitric acid on diisoamyl; it melts at 101·5—102°, is insoluble in water, alkalis, and acids, only sparingly soluble in ether and light petroleum, but readily in benzene, from which it crystallises in long prisms. It sublimes at 100°, is slowly volatilised in a current of steam, and its heat of combustion, calculated on 1 gram-molecule, is 1513614 cal. Since the same compound can be obtained by the further nitration of the previously described tertiary mononitrodiisoamyl it follows that its constitution must be

$$NO_2{\cdot}CMe_2{\cdot}[CH_2]_4{\cdot}CMe_2{\cdot}NO_2.$$

On reduction, it yields a *diamine* which boils at 223—225°. This crystallises when cooled in snow, is fairly readily soluble in water, rapidly absorbs carbonic anhydride from the atmosphere, and is volatile with ether vapour. Its *hydrochloride*, *sulphate*, and *platinochloride* are readily soluble in water, the *oxalate* but sparingly.

II. [With FRL. KIKINA and TSCHITSCHKIN.]—The authors have repeated the experiments of Fittig (*Annalen*, **147**, 2), of Schultz (Abstr., 1884, 904), and of Biedermann and Ledoux (this Journal, 1875, 569), on the nitration of mesitylene, and it is found that in every case, besides the ordinary nitromesitylene mentioned by these authors, an ω-nitromesitylene is also formed. If Schultz's method is adopted, the two compounds are formed in about equal quantities, the other methods yield far less of the ω-compound. *ω-Nitromesitylene* (1 : 3 : 5-xylylnitromethane), $C_6H_3Me_2{\cdot}CH_2{\cdot}NO_2$, is readily soluble in alkalis, from which it can be precipitated by carbonic anhydride, and it melts at 46—47°. It dissolves at the ordinary temperature in fuming nitric acid diluted with twice its volume of glacial acetic acid, but remains unaltered even on warming on the water bath. When treated with 5 parts of nitric acid (sp. gr. = 1·47), this mononitro-compound is converted into *ω-orthodinitromesitylene*,

$$NO_2{\cdot}C_6H_2Me_2{\cdot}CH_2{\cdot}NO_2\ [= 4:1:3:5].$$

It crystallises from benzene in yellowish monoclinic (?) octahedra, melts at 85·5—86°, is only sparingly soluble in alkali carbonates, but readily in alkali hydroxide solutions, yielding orange-red salts. On oxidation, it yields orthonitromesitylenic acid.

On treating the ω-nitromesitylene with a large excess of pure nitric acid, a mixture of two trinitromesitylenes was obtained. The one crystallises from alcohol in large plates or in flat needles, and melts at 117—118·5°. The second could not be obtained in a pure form, but apparently melts between 69° and 73°. They are both readily soluble in alkalis, yielding red salts. The alkali salts of both nitro-compounds give an intensely red precipitate with ferric chloride. Carbonic anhydride and dilute sulphuric acid in the cold precipitate the nitro-compound from solutions of their salts. On oxidation with potassium permanganate, they both yield the corresponding dinitromesitylenic acids, which, however, could not be obtained in a pure state.

These two trinitro-derivatives must have the constitutions

$$C_6HMe_2(NO_2)_2{\cdot}CH_2{\cdot}NO_2\ [= 1:3:2:4:5 \text{ and } 1:3:4:6:5],$$

but the author has not determined which belongs to the lower, and which to the higher, melting nitro-compound.

The heat of combustion per gram-molecule of the isomeric mono- and di-nitromesitylenes was determined with the following results.

| | |
|---|---|
| $C_6H_2Me_3{\cdot}NO_2$ ............ | 1216660 cal. |
| $C_6H_3Me_2{\cdot}CH_2{\cdot}NO_2$........ | 1206332 „ |
| $C_6HMe_3(NO_2)_2$........... | 1186710 „ |
| $NO_2{\cdot}C_6H_2Me_2{\cdot}CH_2{\cdot}NO_2$.... | 1165857 „ |

J. J. S.

**Action of Acids on Salts of Nitro-compounds.** By MICHAEL I. KONOWALOFF (*Ber.*, 1896, **29**, 2193—2198; compare Nef, this vol., i, 460; Hollemann, this vol., i, 148; W. Wislicenus, this vol., i, 369; Hantzsch and Schultze, this vol., i, 353).—The author has previously (*J. Russ. Chem. Soc.*, 1893, i, 513, and 1894, i, 78) drawn attention to the fact that by the action of strong acids, such as nitric, sulphuric, and acetic, on the salts of nitro-compounds in the cold, colourless solid compounds could be obtained. These compounds are more fully described in the present communication.

A *labile* form of *ω-nitromesitylene* has been obtained by the action of dilute sulphuric acid on a solution of the sodium salt of ordinary ω-nitromesitylene (xylylnitromethane) cooled by ice. The precipitated nitro-compound must be filtered at once, and well washed with water, as otherwise it is transformed into a yellow oil. Labile ω-nitromesitylene crystallises from benzene in needles, it is readily soluble in sodium carbonate solutions, and gives a characteristic ferric chloride reaction in alcoholic, ethereal, or benzene solution. It is readily soluble in the above solvents and also in acetone and ethylic acetate, but is only sparingly soluble in light petroleum.

The crystals are readily converted, even at the ordinary temperature, and still more quickly in bright sunlight, into a yellow oil, in which the author has found small quantities of the labile compound, larger quantities of the stable compound, and finally an aldehyde-like substance, which yields a crystalline compound with sodium hydrogen sulphite. The labile compound is fairly stable in ice-cold water; when slowly heated, the substance begins to melt at 50° and is completely melted at 59°; when, however, the substance is placed in a bath already at 61° it does not melt below 63°. A solution of this compound in an alkali hydroxide or carbonate, when treated with sulphuric acid, yields the labile compound unaltered, carbonic anhydride, however, precipitates the stable ω-nitromesitylene.

The freshly prepared sodium salt of diphenylnitromethane also yields a *labile* form of *diphenylnitromethane* when decomposed with dilute sulphuric acid. The crystals are readily soluble in sodium carbonate solution, and give the characteristic reaction with ferric chloride. At the ordinary temperature, the crystals gradually change to a yellowish oil, impurities rendering them even more readily decomposable; the products of decomposition consist of benzophenone, benzophenoneoxime, and the stable nitro-compound. The crystals are, however, stable at low temperatures, and also in ethereal solution.

A *labile phenylisopropylnitromethane* can be obtained in a similar manner, it melts at 54°, and has properties similar to those of the labile compound described above.

The sodium salts of secondary nitrononononaphthene and of secondary nitrodiisoamyl yield liquid labile compounds, and phenylethylnitromethane gives a well crystallised labile isomeride. J. J. S.

**Preparation of Diphenyliodinium Iodide from Iodoxybenzene.** By H. CONRAD C. WILLGERODT (*Ber.*, 1896, **29**, 2008—2009; compare this vol., i, 532).—In the formation of diphenyliodinium iodide from iodoxybenzene and potassium iodide, the solution becomes alkaline and iodine is liberated. It appears probable that the following reactions occur. $PhIO_2 + 2KI + H_2O = PhIO + 2KOH + I_2$; $PhIO + PhIO_2 + KOH = Ph_2I{\cdot}OH + KIO_3$. The hydroxide then reacts with potassium iodide to produce the iodide, which may combine with free iodine to form the periodide, this substance being actually obtained when concentrated solutions are used and only boiled for a short time. Barium hydroxide, in presence of potassium iodide, also produces the iodide. Iodoxybenzene readily dissolves in baryta water, barium iodate being slowly deposited. The filtrate from this only gives a precipitate with potassium iodide after standing for some time. The author is of opinion that iodoxybenzene may be looked on as the anhydride of an iodonic acid, and that the solutions in alkalis contain the salts of this acid, which, however, soon decompose. The question is being further investigated. A. H.

**Derivatives of Phenylic Ether.** By CARL HÄUSSERMANN and EUGEN BAUER (*Ber.*, 1896, **29**, 2083—2085; compare this vol., i, 533). —2 : 4′-*Dinitrophenylic ether* is obtained when the product of the action of parachloronitrobenzene on potassium orthonitrophenol is distilled first in a current of steam, and then under diminished pressure. It forms long, white needles, melts at 103·5°, and is readily soluble in boiling alcohol. When reduced with tin and hydrochloric acid, it yields the *hydrochloride* $(NH_2{\cdot}C_6H_4)_2O,2HCl$, the *free base* of which melts at 78—80°.

2 : 2′-*Dinitrophenylic ether*, obtained from orthochloronitrobenzene and potassium orthonitrophenol, crystallises in white needles, and melts at 114·5°.

*Para-paranitrophenoxybenzoic acid*, $NO_2{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}COOH$, is obtained by adding dipotassium parahydroxybenzoate to an excess of parachloronitrobenzene at 160°; the temperature of the mixture is then gradually raised, and kept at 235° for six hours. The acid crystallises in small, colourless prisms, melts at 236—237°, is insoluble in water, and only sparingly soluble in hot alcohol, ether, and benzene. The *barium* salt crystallises in anhydrous forms, and the *methylic* salt, which crystallises in felted needles, melts at 108—109°, and is readily soluble in benzene.

*Para-paramidophenoxybenzoic acid*, obtained by reducing the nitro-compound with tin and hydrochloric acid, crystallises in yellowish plates, melts at 193—194°, and is very sparingly soluble in water, but more readily in alcohol and in chloroform. It is not decomposed on exposure to the air, and it yields a sparingly soluble *hydrochloride* and *sulphate*. The *barium* salt crystallises in white needles, and the *sodium* salt in silky crystals.

The amido-acid, when diazotised, readily combines with resorcinol, salicylic acid, naphthylaminesulphonic acids, &c., to yield yellow to red dyes.

*Parahydroxyphenylic ether*, obtained from the corresponding amido-ether, crystallises in fine, colourless, felted needles, melts at 84—85°, and is readily soluble in most organic solvents. Its alkaline solution yields a reddish-brown dye with diazobenzene chloride.

J. J. S.

**Duroquinone and the Action of Amido-bases on Quinones.** By LEOPOLD RÜGHEIMER and M. HANKEL (*Ber.*, 1896, **29**, 2171—2175; compare this vol., i, 61).—The author has obtained diamidodurene by reducing the dinitro-derivative with stannous chloride in the presence of alcohol (compare Cain, Abstr., 1895, i, 345); when oxidised with ferric chloride at the ordinary temperature, it yields duroquinone.

The quinone, when heated at 220° for six hours with an excess of aniline, yields duroquinol, but no nitrogenous product could be obtained in a state of purity. That some such product must be formed, in accordance with the views previously expressed (*Annalen*, **287**, 54), follows from the fact, that, however large the excess of aniline used may be, only 50 per cent. of the quinone is converted into the corresponding quinol.

*Duroquinoldiacetate*, $C_6Me_4(OAc)_2$, obtained by heating the quinol with acetic anhydride, crystallises in fine, colourless needles, and melts at 202—203°. The *dipropionate* melts at 138·5—139·5°.

J. J. S.

**Action of Ammonia and Amines on Bisulphides.** By MAX BUSCH and ALFRED STERN (*Ber.*, 1896, **29**, 2148—2151).—Whilst phenylic and benzylic bisulphides resist the action of alcoholic ammonia or aniline at temperatures approaching 250°, benzoic bisulphide, under the influence of cold alcoholic ammonia gives rise to ammonium thiobenzoate, sulphur, and benzamide; the action of alcoholic aniline converts it into benzanilide, with liberation of hydrogen sulphide and sulphur.

The *bisulphide* of phenylthiocarbazinic acid, $S_2(CS{\cdot}NH{\cdot}NHPh)$ is obtained by the action of an alcoholic solution of iodine on potassium phenylthiocarbazinate, forming a yellow powder, which dissolves with great difficulty in ordinary solvents; alcoholic ammonia converts it in phenylthiosemicarbazide, ammonium phenylthiocarbazinate and sulphur being also produced. M. O. F.

**Benzylideneimide.** By MAX BUSCH (*Ber.*, 1896, **29**, 2143—2148; compare this vol., i, 705).—*Benzylideneimide hydrochloride*,

$$CHPh{:}NH,HCl,$$

which crystallises in snow-white, lustrous leaflets, is obtained by the action of alcoholic hydrogen chloride on phenyldithiobiazolone benzylidenesulphime; it is, however, more conveniently prepared by leading dry hydrogen chloride over a continuously agitated solution of hydrobenzamide in benzene to which absolute alcohol (2 mols.) has been added, until absorption ceases, the temperature of the liquid being maintained meanwhile at 5°. The salt melts at 181°, yields ammonium chloride and benzaldehyde on treatment with water, and ammonium chloride and benzylidene diethyl ether under the influence of alcohol; it crystallises from glacial acetic acid in silvery leaflets. On treating benzylideneimide hydrochloride with alkalis, in order to obtain the free base, ammonia is liberated and hydrobenzamide is produced; ammonia and pyridine produce the same effect, whilst primary amines and hydrazines give rise to benzylidene derivatives and hydrazones respectively.

*Benzylideneimide sulphate* crystallises in silvery leaflets, becoming reddish if kept, and melts at 144°; in properties and behaviour towards various agents, it closely resembles the hydrochloride.

M. O. F.

**Action of Diazo-compounds on Tartrazin.** By ROBERT GNEHM and LOUIS BENDA (*Ber.*, 1896, **29**, 2017—2019).—When a solution of paranitrodiazobenzene chloride is added to an alkaline solution of tartrazin, nitrogen is evolved, and a substance is formed which crystallises in yellow needles, and decomposes when strongly heated leaving a voluminous residue. It dyes wool, in an acid bath, a fine orange shade, very fast to light. This substance probably has the constitution

$$NO_2\cdot C_6H_4\cdot NH\cdot N\colon C(COOH)\cdot C(COOH)\colon N\cdot NH\cdot C_6H_4\cdot SO_3Na.$$

It can also be obtained from dihydroxytartaric acid, paranitrophenylhydrazine and paraphenylhydrazinesulphonic acid. The nitrogen which is evolved is a secondary product, and arises from the decomposition of the paradiazobenzenesulphonic acid which is formed in the reaction.

A. H.

**Diazomethanedisulphonic acid.** By HANS VON PECHMANN (*Ber.*, 1896, **29**, 2161—2169; compare this vol., i, 14).—*Potassium azinemethanedisulphonate*, $C(SO_3K)_2\colon N\cdot N\colon C(SO_3K)_2$, is obtained by dehydrating powdered dipotassium diazomethanedisulphonate (*loc. cit.*) in an atmosphere of hydrogen at 100°, and heating it in xylene for 10—12 hours at 120—130°; it crystallises from water in rosettes of white prisms, and contains $2H_2O$. The action of boiling acids on the substance liberates sulphurous anhydride, and gives rise to the production of hydrazine, whilst a solution of barium chloride yields a precipitate which dissolves in excess of the agent, lustrous leaflets, which do not redissolve when heated, separating from the liquid obtained in this way.

*Ethylic glyoxylate phenylhydrazone*, $COOEt\cdot CH\colon N\cdot NHPh$, is produced when a slightly acid solution of diazobenzeneacetate is added to a solution of potassium ethylic sulphohydrazimethylenecarboxylate (Abstr., 1895, i, 642) at 0°; it crystallises from dilute alcohol in colourless, rhombic leaflets, and melts at 130—131°. The solution in concentrated sulphuric acid is yellow, and develops a reddish-violet coloration with ferric chloride or potassium dichromate; alcoholic soda acts on it hydrolytically, producing the phenylhydrazone of glyoxylic acid.

*Ethylic formazylformate*, $NH_2\cdot N\colon C(N_2Ph)\cdot COOEt$, is obtained by the action of an alkaline solution of diazobenzene (2 mols.) on potassium ethylic sulphohydrazimethylenecarboxylate at 0°; it crystallises from alcohol in leaflets, and melts at 117°. Hydrolysis converts it into formazylformic acid (m. p. 162°).

*Potassium phenylhydrazonemethanedisulphonate*, $C(SO_3K)_2\colon N\cdot NHPh$, is produced when a concentrated solution of diazobenzene acetate ($1\frac{1}{2}$ mol.) is added to the additive sulphite compound of dipotassium diazomethanedisulphonate dissolved in 8 parts of water; after 12 hours, inorganic salts having been removed, and sulphuric acid exactly precipitated with barium acetate, the solution is concentrated. The dipotassium salt crystallises from alcohol or water in flat, lustrous needles; the solution in concentrated sulphuric acid develops a violet coloration with ferric chloride or potassium chromate. Hot acids resolve it into sulphurous anhydride and phenylhydrazine, and sulphurous acid converts it into a *compound* which is volatile in steam, crystallises in slender needles melting at 88—90°, and is free from sulphur.

*Potassium diazobenzenephenylhydrazonemethanedisulphonate*,

$$(SO_3K)_2C\colon N\cdot NPh\cdot N\colon NPh,$$

is obtained from the foregoing salt and diazobenzene; it crystallises in slender, orange-yellow needles which darken on exposure to light, and explodes at 180°. Concentrated sulphuric acid dissolves it with a violet coloration, and mercuric nitrate produces a purple precipitate; alkaline reducing agents develop an intense red coloration, which is fugitive. A solution of the diazoamido-salt is decolorised by cold, dilute acids, alcohol precipitating the original hydrazone; if the liquid is treated with alkali, however, the diazoamido-salt is precipitated. After a short interval, a neutral or alkaline aqueous solution deposits slender needles which melt at 187°, and the liquid contains dipotassium phenylhydrazonemethanedisulphonate and potassium benzenediazosulphonate.

*Formazylsulphonic acid*, $NHPh\cdot N\colon C(N_2Ph)\cdot SO_3H$, is obtained by suspending finely divided potassium diazobenzenephenylhydrazonemethanedisulphonate in 10 parts of alcohol, and adding alcoholic hydrochloric acid to the cooled solution. It crystallises from ethylic acetate in violet leaflets having a blue reflex, and sinters at 192°; the solution in concentrated sulphuric acid is blue, and becomes violet on the addition of nitric acid. Boiling dilute acids give rise to sulphurous anhydride and phenylhydrazine, and reducing agents convert it into potassium phenylhydrazonemethanedisulphonate, along with aniline and phenylhydrazine. The *potassium* salt crystallises from much boiling alcohol, and forms red, lustrous needles.

*Potassium parabromodiazobenzenephenylhydrazonemethanedisulphonate*, $C(SO_3K)_2\colon N\cdot NPh\cdot N\colon N\cdot C_6H_4Br$, is prepared from dipotassium phenylhydrazonemethanedisulphonate and parabromodiazobenzene in alkaline solution; it forms sparingly soluble, orange-yellow needles.

*Parabromoformazylsulphonic acid*, $NHPh{\cdot}N{:}C(N_2{\cdot}C_6H_4Br){\cdot}SO_3H$, is produced when the foregoing substance is treated with alcoholic hydrochloric acid; it crystallises from ethylic acetate in violet scales, and sinters at 196°.

*Benzoylhydrazonepyruvic acid*, $NHBz{\cdot}N{:}CMe{\cdot}COOH$, is obtained by the action of dilute pyruvic acid on a hot, aqueous solution of benzoylhydrazine, and crystallises from boiling water or dilute alcohol in colourless needles which melt at 112°; it contains $1H_2O$, becoming anhydrous at 110—115°, and in this condition melts at 155°. Pyruvic acid is eliminated from the substance under the influence of diazobenzene or the additive sulphite compounds of aliphatic diazo-compounds. Paranitrodiazobenzene has the same effect, converting it into a substance which is probably *paranitrodiazobenzenebenzoylhydrazine*, $NHBz{\cdot}NH{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2$; this forms a lemon-yellow precipitate, and cannot be recrystallised, as boiling water or alcohol converts it into benzamide and *paranitrodiazobenzeneimide*,

$$\begin{matrix}N\\ \|\\ N\end{matrix}{>}N{\cdot}C_6H_4{\cdot}NO_2,$$

which crystallises from petroleum in yellowish leaflets, and melts at 71—72°. The latter substance is readily formed by the action of nitrodiazobenzene on hydrazine dissolved in acetic acid, in presence of ammonia; it is volatile in an atmosphere of steam.

M. O. F.

### Hydrazides and Azides [Azoimides] of the Phthalic acids.

By THEODOR CURTIUS and ERNST DAVIDIS (*J. pr. Chem.*, 1896, [2], **54**, 66—87).—The phthalylhydrazide prepared by the action of hydrazine hydrate on ethylic phthalate and on phthalic chloride is identical with that prepared from phthalic anhydride (Abstr., 1895, i, 354); the crystallography of the compound is given.

*Isophthalylhydrazide*, $C_6H_4(CON_2H_3)_2$, is prepared by dissolving ethylic isophthalate (1 mol.) and hydrazine hydrate (1 mol.) in absolute alcohol, and heating on the water bath for four hours; the powder which separates on cooling is crystallised from 80 per cent. alcohol. The hydrazide forms white, silky needles, melting at 220°; it dissolves easily in warm water, dilute alcohol, and glacial acetic acid, more sparingly in absolute alcohol, but not in ether or benzene. It reduces Fehling's solution, ammoniacal silver nitrate, and platinic chloride in the cold. Prolonged heating with acids decomposes it into isophthalic acid and a hydrazine salt. The *hydrochloride*, $C_8H_{10}N_4O_2,2HCl$, and the *platinosochloride*, $C_8H_{10}N_4O_2,H_2PtCl_4$, are described. The *acetone* [*isopropylidene*] derivative,

$$C_6H_4(CO{\cdot}NH{\cdot}N{:}CMe_2)_2,$$

crystallises in slender needles, melts at 243—244°, and is freely soluble in absolute alcohol and ether. The *benzylidene* derivative, $C_6H_4(CO{\cdot}NH{\cdot}N{:}CHPh)_2$, formed by treating the hydrazide with benzaldehyde, crystallises in colourless needles, melts at 241°, and dissolves sparingly in alcohol and water, but not in ether.

*Ethylic isophthalylhydrazidacetoacetate*,

$$C_6H_4(CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}COOEt)_2,$$

prepared by warming isophthalylhydrazide with ethylic acetoacetate, crystallises with difficulty, melts at 145°, and is extraordinarily soluble in alcohol.

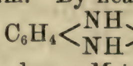
*Isophthalazoimide*, $C_6H_4(CON_3)_2$, prepared by diazotising the hydrazide, crystallises in transparent, anisotropic prisms, melts at 56°, and is freely soluble in ether and acetone; when dry it is somewhat explosive.

When ethylic terephthalate and hydrazine hydrate are heated together on the water bath, only one ethoxy-group is substituted, *ethylic terephthalylhydrazinate*, $NH_2{\cdot}NH{\cdot}C_6H_4{\cdot}COOEt$, being produced in whatever proportions the reacting compounds are mixed. The salt crystallises in slender, white needles, melts at 164—165°, and dissolves freely in hot water, alcohol, and glacial acetic acid, but not in ether. It is less stable than isophthalylhydrazide, and has similar reducing properties. The *hydrochloride*, $C_{10}H_{12}N_2O_3,HCl$, and the *sodium* derivative, $C_{10}H_{11}N_2O_3Na$, are described. The *benzylidene derivative* crystallises in slender, colourless needles, and melts at 259°.

*Ethylic terephthalylazoimate*, $N_3{\cdot}CO{\cdot}C_6H_4{\cdot}COOEt$, obtained by diazotising the hydrazide, crystallises in colourless tables which have an irritating, aromatic odour, melt at the temperature of the hand, and dissolve freely in ether and acetone.

*Terephthalylhydrazide*, $C_6H_4(CON_2H_3)_2$, is prepared by heating ethylic or methylic terephthalate (1 mol.) with hydrazine hydrate (2 mols.) and some alcohol for 3 to 4 hours in a tube at 130—140°. It crystallises in small, felted needles, melts above 300°, and is very sparingly soluble. The *hydrochloride*, $C_8H_{10}N_4O_2,2HCl$, the *benzylidene* derivative, and the *acetone* [*isopropylidene*] derivative (m. p. 261—262°) are described. *Ethylic terephthalylhydrazidacetoacetate*, $C_6H_4(CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}COOEt)_2$, forms yellowish granular crystals, and melts at 240°.

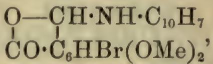
*Formylideneterephthalylhydrazide*, $C_6H_4(CO{\cdot}NH{\cdot}N{:}CH_2)_2$, from formaldehyde and the hydrazide, is a grey, insoluble powder; it does not melt at 300°.

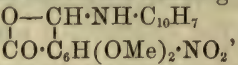
*Terephthalazoimide*, $C_6H_4(CON_3)_2$, prepared like isophthalazoimide, crystallises in colourless tables, melts at 110°, and is freely soluble in ether and acetone. When suspended in dry alcohol and gently warmed until evolution of gas ceases, it is converted into *paraphenylenethylurethane*, $C_6H_4(NH{\cdot}COOEt)_2$, which crystallises in colourless tables, melts at 195°, and is freely soluble in alcohol, ether, benzene, chloroform, and light petroleum. By heating terephthalazide with water, *paraphenylenecarbamide*,  $C_6H_4{<}{}^{NH}_{NH}{>}CO$, is obtained as a reddish, insoluble, crystalline powder. *Metaphenylenethylurethane*, prepared from isophthalazide in the manner indicated for the para-compound, crystallises in small tables, melts at 143—145°, and shows a solu-

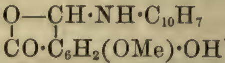
bility similar to that of the para-compound. Metaphenylenecarbamide has been prepared by Michler and Zimmerman (Abstr., 1882, 182).
A. G. B.

**[Bromocinnamic Acids: Alloisomerism.]** By ARTHUR MICHAEL (*J. pr. Chem.*, 1896, [2], **54**, 107—112).—Comments of a purely controversial character on Erlenmeyer's recent paper (this vol., i, 46), and a reply to the criticisms of Liebermann (this vol., i, 347).
A. G. B.

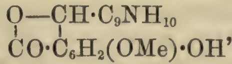
**Tautomerism of the Orthoaldehydic Acids. II.** By CARL T. LIEBERMANN (*Ber.*, 1896, **29**, 2030—2036; compare this vol., i, 232).—The behaviour of orthoaldehydic acids towards bases was further studied with the object of ascertaining in which of their tautomeric modifications they most frequently appeared. Bromo- and nitro-opianic acids behaved towards primary and secondary bases as hydroxyphthalides; the compounds of the former with primary bases, which at first appeared to be more readily changed to the aldehydic acid modification than those of opianic acid itself, are now known to be equally stable. It is better to continue the shaking with soda during a longer period, but 15 minutes suffices to cause the greater portion of the compound to dissolve. Soon after dissolution, however, the excess of soda effects a partial decomposition into base and acid; the liquid is, therefore, quickly filtered and acidified with acetic acid which causes the precipitation of an acid having the normal constitution $COOH\cdot\overset{|}{C}H\cdot\overset{|}{C}H\cdot CH{:}NR$. The compounds of the latter type, when damp, dissolve immediately in one per cent. soda solution, but after drying show their original behaviour. Suspecting the existence of compounds intermediate between the above two types, the author has subjected opianic acid β-naphthylamine to careful treatment with soda, &c., but has not succeeded in obtaining evidence of the production of any such substance.

*Bromopianic acid β-naphthylamide,*  $\begin{array}{l}O\text{—}CH\cdot NH\cdot C_{10}H_7\\ |\qquad |\\ CO\cdot C_6HBr(OMe)_2\end{array}$, melts at 213°, and dissolves in cold soda after continued shaking.

*Nitropianic acid β-naphthylamide,*  $\begin{array}{l}O\text{—}CH\cdot NH\cdot C_{10}H_7\\ |\qquad |\\ CO\cdot C_6H(OMe)_2\cdot NO_2\end{array}$, is very sparingly soluble in alcohol, and melts and decomposes at about 232°. It is insoluble in cold soda, but dissolves, on warming, with production of the sodium salt of nitropian-β-naphthylamic acid.

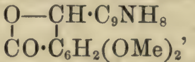
Methylnoropianic acid melts, not at 140—142°, but at 155—156°, or, when containing water of crystallisation, at about 100°. *Methylnoropian-β-naphthalidic acid* (?),
$COOH\cdot C_6H_2(OH)(OMe)\cdot CH{:}N\cdot C_{10}H_7(\beta)$ ?, or  $\begin{array}{l}O\text{—}CH\cdot NH\cdot C_{10}H_7\\ |\qquad |\\ CO\cdot C_6H_2(OMe)\cdot OH\end{array}$, is obtained as a beautiful, lemon-yellow crystalline precipitate, on mixing its constituents. It melts and decomposes at about 225°, and dissolves readily in cold soda with production of the sodium salt; the latter, when decomposed by dilute acetic acid, yields

the original substance in yellow, caseous masses. α-Naphthylamine, aniline, and paratoluidine yield similar compounds with methylnoropianic acid; the *aniline* derivative melts and decomposes at 199°, and the *paratoluidine* derivative at 211°. The *sodium* salt of methylnoropiananilidic acid seems to contain 1 mol. $H_2O$, which is lost at 75—105°. *Methylnoropianic acid tetrahydroquinoline*,

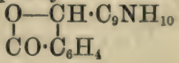
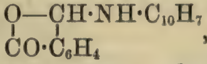


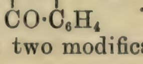
$$\begin{array}{l} O\text{—}CH\cdot C_9NH_{10} \\ | \qquad | \\ CO\cdot C_6H_2(OMe)\cdot OH' \end{array}$$

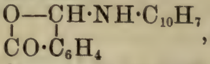
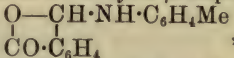
separates, on mixing cold alcoholic solutions of its components, in long, white leaflets, being subsequently sparingly soluble in alcohol. When treated with soda, it suddenly coagulates, an effect probably due to the production of a sodium salt. It melts at 231°.

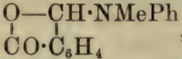
*Opianic acid methylketolide*,  $\begin{array}{l} O\text{—}CH\cdot C_9NH_8 \\ | \qquad | \\ CO\cdot C_6H_2(OMe)_2 \end{array}$, prepared by the interaction of opianic acid and methylketole, forms silky needles melting at 194°, and is insoluble in soda and strong hydrochloric acid. *Opiananthranilic acid*, $COOH\cdot C_6H_2(OMe)_2\cdot CH{:}N\cdot C_6H_4\cdot COOH$, melts at 231°, and dissolves in soda, being reprecipitated unchanged on the addition of acetic acid. Analyses of the barium and calcium salts are in agreement with the above formula.

Tertiary aromatic bases do not yield anhydro-compounds with opianic acid, and, when these mixed solutions in acetone are evaporated, ether separates the base from the sparingly soluble opianic acid. ψ-Tropine, however, combines with opianic acid in acetone solution with production of beautiful, lustrous crystals of *ψ-tropine opianate*, $C_8H_{15}NO,C_{10}H_{10}O_5$; the latter dissolves readily in water, and is at once decomposed by dilute alkalis or acids, its constituents being regenerated. ψ-Tropine may be separated from tropine by this means. A. L.

**Orthophthalaldehydic Acid and Aromatic Bases.** By R. GLOGAUER (*Ber.*, 1896, **29**, 2036—2039; compare preceding Abstract).—Racine (Abstr., 1887, 951) has shown that orthophthaldehydic acid combines with aniline with production of a substance, having acid properties, to which he ascribes the formula $COOH\cdot C_6H_4\cdot CH{:}NPh$; Liebermann, on the other hand, has observed (this vol., i, 232) that its compounds with tetrahydroquinoline, and β-naphthylamine are insoluble in soda, and may be assigned the formulæ  $\begin{array}{l} O\text{—}CH\cdot C_9NH_{10} \\ | \qquad | \\ CO\cdot C_6H_4 \end{array}$ and  $\begin{array}{l} O\text{—}CH\cdot NH\cdot C_{10}H_7 \\ | \qquad | \\ CO\cdot C_6H_4 \end{array}$, respectively.

In all instances observed by the author, the action may be represented by the scheme:—1 mol. acid + 1 mol. base − 1 mol. water. The compounds with secondary bases are invariably insoluble in cold soda, but are decomposed into acid and base on warming; they, therefore, pertain to the hydroxyphthalide type,  $\begin{array}{l} O\text{—}CH\cdot NR_2 \\ | \qquad | \\ CO\cdot C_6H_4 \end{array}$. The compounds with primary bases usually exist in two modifications, and as the aniline compound dissolves rapidly in soda, the formula assigned to it by Racine is doubtless the correct one.

*Phthalaldehydic-α-naphthylamide,*  $\begin{array}{l} O—CH\cdot NH\cdot C_{10}H_7 \\ \,|\quad\;\; | \\ CO\cdot C_6H_4 \end{array}$, is soluble with difficulty in aqueous soda, and melts at 155—159°. *Phthalaldehyde-α-naphthylamic acid,* $COOH\cdot C_6H_4\cdot CH{:}N\cdot C_{10}H_7$, prepared by dissolving the preceding substance in dilute soda and precipitating with acetic acid, is readily soluble in soda. Phthalaldehydic-β-naphthylamide is dissolved very slowly by soda with production of the readily soluble phthalaldehyde-β-naphthylamic acid. *Phthalaldehydic-paratoluidide,*  $\begin{array}{l} O—CH\cdot NH\cdot C_6H_4Me \\ \,|\quad\;\; | \\ CO\cdot C_6H_4 \end{array}$, melts at 149°, and after continued shaking with soda yields *phthalaldehydeparatoluidic acid,* $COOH\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4Me$.

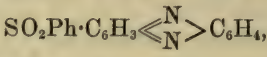
*Phthalaldehydemethylanilide,*  $\begin{array}{l} O—CH\cdot NMePh \\ \,|\quad\;\; | \\ CO\cdot C_6H_4 \end{array}$, crystallises from alcohol and melts at 150°; it is insoluble in soda but is decomposed by ammonia, phthalaldehydic acid and methylaniline being regenerated. *Phthalaldehydic-tetrahydroisoquinolide* melts at 170°, whilst *phthalaldehydic-piperidide,* crystallises from ether in needles melting at 97°. A. L.

**Paratoluenesulphinic acid.** By ERNST VON MEYER (*J. pr. Chem.*, 1896, [2], **54**, 95—97; compare Piloty, this vol., i, 555).—When ditoluenesulphonylhydroxylamide, $OH\cdot N(SO_2\cdot C_7H_7)_2$ (König, Abstr., 1878, 573), is mixed with paratoluenesulphinic acid in glacial acetic acid solution, *tritoluenesulphonamide,* $(C_7H_7SO_2)_3N$, is obtained; this forms white crystals and melts at 186°. Paratoluenesulphinic acid combines with formaldehyde yielding *paratolylhydroxymethylsulphone,* $C_7H_7\cdot SO_2\cdot CH_2\cdot OH$, which melts at 90°. In an ether-alcohol solution of paratoluenesulphinic acid, ammonia precipitates the ammonium salt, which decomposes and melts at 175°; but, in a benzene solution, in the absence of water, an intramolecular decomposition occurs with formation of ammonium paratoluenesulphonate and "paratoluenedisulphoxide," $C_7H_7SO_2\cdot SC_7H_7$.

*Aniline paratoluenesulphinate* melts at 118°, and at 160° loses water together with some toluene and sulphurous anhydride; the residue yields to alcohol a substance which dissolves with a brilliant blue-violet colour and behaves as an unstable dye.

Well crystallised compounds are obtained from paratoluenesulphinic acid and phenylhydrazine and hydrazine hydrate respectively. The research is proceeding. A. G. B.

**Benzenesulphinic acid as a Reagent.** By OSCAR HINSBERG and A. HIMMELSCHEIN (*Ber.*, 1896, **29**, 2019—2023; compare Abstr., 1895, i, 144 and 471).—*Phenazylphenylsulphone,*



$$SO_2Ph\cdot C_6H_3{\lessdot}\begin{smallmatrix}N\\N\end{smallmatrix}{>}C_6H_4,$$

prepared by the action of phenazine on benzenesulphinic acid in presence of hydrochloric acid at 30—40°, crystallises in bright yellow, glistening leaflets, and melts at 244° (uncorr.). It is nearly insoluble in water, but dissolves slightly in alcohol and readily in acetic acid. Its solutions in concentrated sulphuric and hydrochloric acids contain the corresponding salts, but these are decomposed on the addition of water, the sulphone being precipitated. It is not affected by alkalis at 100°, but is reduced to phenylic hydrosulphide by zinc and warm hydrochloric acid. When prepared in the above manner, it is accompanied by the hydrochloride of phenazine and dihydrophenazine, and a small quantity of a substance melting at about 275° and sparingly soluble in acetic acid, probably the disulphone $C_{12}H_6N_2(SO_2Ph)_2$.

*Paramidotolylphenylsulphone*, $SO_2Ph{\cdot}C_6H_3Me{\cdot}NH_2$, is obtained when paramidobenzylic alcohol, or its anhydride, is warmed with dilute hydrochloric acid, and the dark yellow solution of the compound thus obtained (compare Abstr., 1895, i, 299) is mixed with benzenesulphinic acid. It dissolves readily in hot water, forming a colourless solution; the crystals deposited on cooling are colourless, but become yellow on drying, and melt at 176°. It dissolves sparingly in alcohol and glacial acetic acid, forming, in the latter instance, a yellow solution. It gives a colourless, stable hydrochloride, and yields a colourless diazo-compound which reacts with sodium naphthoxide, forming an orange dye. The *acetyl* derivative, $SO_2Ph{\cdot}C_6H_3Me{\cdot}NHAc$, is sparingly soluble in water, but dissolves readily in acetic acid and alcohol, and crystallises in colourless needles melting at 201°.

Rosaniline salts do not readily react with benzenesulphinic acid.

A. L.

**Hydroxy- and Amido-derivatives of Diphenylsulphone.** By OSCAR HINSBERG and A. HIMMELSCHEIN (*Ber.*, 1896, **29**, 2023—2029). —It is well known that when the ortho- and para-dihydroxy-, diamido- and amido-hydroxy-benzenes, are oxidised with acid reagents, they all, with the exception of quinol, yield coloured substances of complex structure. As it appeared possible that simple derivatives of ortho- and para-quinones were the initial products, the authors have carried out the oxidation of several such di-derivatives of benzene in presence of benzenesulphinic acid which eagerly combines with quinonoïd compounds, and, as was expected, instead of highly coloured products, colourless substances were obtained.

Quinol, when oxidised with a cold aqueous solution of potassium dichromate in presence of benzenesulphinic acid, yields 1 : 4-dihydroxyphenylsulphone. Catechol, when treated in a similar manner, gives a bright green chromium compound, from which, by treatment with acetic acid, chromium acetate and 1 : 2-*dihydroxyphenylparaphenylsulphone*, $SO_2Ph{\cdot}C_6H_3(OH)_2$, are obtained. The latter, when crystallised from water, contains water of crystallisation which it loses above 110°; the dried substance melts at about 164°, dissolves readily in hot water, alcohol, and acetic acid, and its solutions in alkalis are yellow. Its aqueous solution, when mixed with ferric chloride, gives a bluish-green coloration, changed to red by soda.

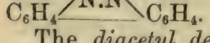
*Trihydroxyphenylsulphone*, $SO_2Ph{\cdot}C_6H_2(OH)_3$ $[(OH)_3 = 1 : 2 : 3]$, prepared from pyrogallol and benzenesulphinic acid, crystallises from hot water in large, colourless tablets melting at 188°. It dissolves readily in hot water and alcohol, but is sparingly soluble in ether; ferric chloride produces in its aqueous solution a deep blue colour, changed to red by soda; its alkaline salts give deep yellow solutions. It gives a bluish-black tint to cloth steeped in iron salts.

3 : 5-*Diphenyldisulphoneparaphenylenediamine*, $C_6H_2(NH_2)_2(SO_2Ph)_2$, is obtained when paraphenylenediamine is oxidised in acid solution by potassium dichromate in presence of benzenesulphinic acid. It separates from chloroform, on the addition of light petroleum, as a yellow, crystalline precipitate composed of microscopic needles; it is nearly insoluble in water, and sparingly soluble in ether, but dissolves readily in alcohol and acetic acid, and melts at 115° forming a viscid liquid. When treated with strong hydrochloric or sulphuric acid, it yields colourless salts which are prone to oxidation, assuming a violet colour when exposed to the air. When oxidised in acetic acid solution by potassium dichromate, it yields a red base whose salts are violet. The sulphone, when treated with acetic anhydride, yields a colourless *acetyl* derivative, $C_{18}H_{16}N_2S_2O_4$.

When paramidodimethylaniline is oxidised in presence of benzenesulphinic acid, it yields the same diphenyldisulphonedimethylparaphenylenediamine as is obtained by the direct interaction of nitrosodimethylaniline hydrochloride and benzenesulphinic acid (compare Abstr., 1895, i, 144).

*Diphenylsulphoneorthamidophenol*, $OH{\cdot}C_6H_2(SO_2Ph)_2{\cdot}NH_2$, is obtained by the oxidation of orthamidophenol in presence of benzenesulphinic acid; water precipitates it from its solution in acetic acid as a yellowish, crystalline mass, which melts, after showing signs of sintering, at about 115°, forming a dark liquid; it is sparingly soluble in water, but is readily dissolved by alcohol and acetic acid; its *sodium* salt dissolves in water, yielding a pure yellow solution from which it is reprecipitated by excess of strong soda. The *hydrochloride* of the disulphone is a yellowish-brown substance which is decomposed by water. A. L.

**Diorthodiamidodiphenyl.** By ERNST TÄUBER (*Ber.*, 1896, **29**, 2270—2272).—Diphenyleneorthodihydrazine (Abstr., 1893, i, 588) crystallises in yellowish plates melting at 110°. The *hydrochloride* forms lustrous plates, and the *sulphate* sparingly soluble tablets. At 150°, the hydrazine is converted quantitatively into *diphenyleneazone*,



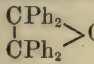
$C_6H_4\diagup\overset{N:N}{\underline{\qquad}}\diagdown C_6H_4$.

The *diacetyl derivative* is only very slightly soluble in the usual solvents, and, when heated, decomposes with formation of acetamide and diphenyleneazone. A. H.

**Benzhydrol Ether and the Benzopinacolins.** By HEINRICH KLINGER and CARL LONNES (*Ber.*, 1896, **29**, 2158—2160).—The compound, $C_{26}H_{20}O$, obtained on melting benzopinacone, was regarded by Thörner and Zincke as identical with benzhydrol ether, which, according to Linnemann, has the formula $C_{26}H_{22}O$ (*Annalen*, 1865, **133**, 6). The authors have, therefore, prepared benzhydrol ether by three different methods—heating benzhydrol at its boiling point, heating it with benzylic acid, and heating it with dilute sulphuric acid at 180°; in each case the product melts at 109°, and has the formula $C_{26}H_{22}O$. The substance does not yield β-benzopinacolin under the influence of hot acetic chloride, and, as the compound described by Thörner and Zincke undergoes the change in question, the two substances can no longer be regarded as identical.

Although Delacre has ascribed to α-benzopinacolin the bimolecular formula, $C_{52}H_{40}O_2$ (*Bull. Acad. Roy. Belg.*, [3], **21**, 541), an ebullioscopic determination of the molecular weight in acetone establishes the formula $C_{26}H_{20}O$. The compound, obtained by reducing α-benzopinacolin with sodium and amylic alcohol, and represented by Delacre as having the composition $C_{52}H_{42}O$, melts at 210°, and has all the properties of tetraphenylethane.

β-Benzopinacolin also has the formula $C_{26}H_{20}O$, and the two isomerides must be, therefore, represented respectively by the expressions



$\begin{matrix}CPh_2\\ | \\ CPh_2\end{matrix}\!>O$ and $CPh_3\cdot COPh$. M. O. F.

**Two Isomeric Bromodiphenacyls.** By CARL PAAL and KARL DEMELER (*Ber.*, 1896, **29**, 2092—2097).—During an attempt to produce ethylic diphenacylacetoacetate in more remunerative quantity, a mixture of two compounds, having the formula $C_{16}H_{13}BrO_2$, has been obtained; both substances yield diphenacyl on reduction, and one modification is transformed into the isomeride when the alcoholic solution is boiled. The compounds are, therefore, isomeric forms of bromodiphenacyl, a substance which the authors, consequently, regard as capable of existing in both its ketonic and enolic forms (compare Claisen, this vol., i, 557); the possibility of stereoisomerism, however, also presents itself.

*Bromodiphenacyl*, $C_{16}H_{13}BrO_2$, melting at 129°, is obtained by the action of phenacyl bromide on ethylic sodioacetoacetate, and separated, along with the isomeride, by treating the product with cold, six per cent., aqueous potash, in which they do not dissolve; it is more conveniently prepared, however, by the method which Fritz describes for obtaining the isomeride melting at 161° (this vol., i, 152), namely, treatment of an ice-cold, alcoholic solution of bromacetophenone with sodium and alcohol. The authors have found that the sole product of this action is the modification of low melting point; only after protracted boiling has the less fusible form been obtained by this method, and then only in quantity amounting to one-third of the whole product. The explanation of this discrepancy is probably to be found in the fact that the modification of low melting point is converted into the isomeride when the alcoholic solution is boiled.

Bromodiphenacyl, melting at 161°, has been already described by Fritz (*loc. cit.*), and, owing to the discrepancy indicated, is most conveniently obtained by the action of phenacyl bromide on ethylic sodioacetoacetate. M. O. F.

**Diduroquinone.** By LEOPOLD RÜGHEIMER and M. HANKEL (*Ber.*, 1896, **29**, 2176—2185).—Duroquinone (see this vol., i, 677), on treatment with a 5—10 per cent. alcoholic potash solution at the ordinary temperature is slowly polymerised to *diduroquinone*, $C_6Me_3O_2·CH_2·C_6Me_4O·OH$, which crystallises from its alcoholic solution in small, yellow needles, melts at 202—203°, is only sparingly soluble in cold alcohol and benzene, but dissolves in alcoholic potash yielding a violet solution; it is not acted on when heated at 100° with alcohol previously acidified with hydrogen chloride, or by prolonged heating with alcoholic potash.

*Diduroquinone ethylic ether*, $C_{20}H_{23}O_3·OEt$, obtained by heating a solution of the diquinone in alcoholic potash with ethylic iodide, crystallises in yellow needles, and melts at 128—130°; it is not acted on by acetic anhydride at 190°, and, on reduction with zinc dust and acetic acid yields duroquinol. *Diduroquinone methylic ether* crystallises from hot alcohol in small, yellow needles, and melts at 126°. *Diduroquinone propylic ether* melts at 116°. *Acetyldiduroquinone*, obtained by the action of acetic anhydride on the diquinone, crystallises from its alcoholic solution with 1 mol. of alcohol; it loses half this alcohol at 100°, but does not lose the other ½ mol. at 120°. The air-dried crystals melt at 128—132°, when dried at 100° they melt at 133—134°. *Benzoyldiduroquinone* melts at 140—142°.

Diduroquinone, when reduced in alcoholic solution with aluminium amalgam, yields a *dihydro*-derivative, which is rapidly oxidised again to the diquinone by contact with the air; on treatment with acetic anhydride, it yields a *monacetyl* derivative melting at 153°.

J. J. S.

**Action of Benzaldehyde on Paratolyl Methyl Ketone.** By STANISLAUS VON KOSTANECKI and G. ROSSBACH (*Ber.*, 1896, **29**, 2245—2247; compare this vol., i, 556).—Dibenzylidenetriacetophenone is formed with great ease, even in the presence of dilute aqueous soda, if this reagent is allowed to act on the mixture for a considerable time. Paratolyl methyl ketone, on the other hand, does not form the tri-compound nearly so readily.

*Paratolyl styryl ketone* (*paratolyl benzylidenemethyl ketone*),

$$CHPh{:}CH·CO·C_6H_4Me,$$

crystallises in long, thick needles, melts at 77°, and boils at 355°. Sulphuric acid colours it yellow. *Diparatolyl benzylidenedimethyl diketone*, $CHPh(CH_2·CO·C_6H_4Me)_2$, forms vitreous prisms melting at 115—116°. It yields a colourless solution in sulphuric acid, which, however, soon becomes yellowish, and takes a greenish fluorescence. *Dibenzylidenetrimethyl triparatolyl triketone*,

$$C_6H_4Me·CO·CH(CHPh·CH_2·CO·C_6H_4Me)_2,$$

is a crystalline powder, which melts at 228°, and is only sparingly soluble in alcohol. It dissolves in sulphuric acid, forming a red solution which has a cinnabar-red fluorescence. A. H.

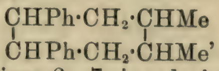
**Action of Furfuraldehyde on Acetophenone.** By STANISLAUS VON KOSTANECKI and L. PODRAJANSKY (*Ber.*, 1896, **29**, 2248—2250).—Furfuraldehyde acts on acetophenone in a manner similar to benzaldehyde. *Furfurylideneacetophenone*, $C_4OH_3·CH{:}CH·COPh$, is a thick, yellowish oil, which boils at 317°, and is coloured brown by sulphuric acid. *Furfurylidenediacetophenone*, $C_4OH_3\cdot CH(CH_2\cdot COPh)_2$, crystallises in lustrous, prismatic needles, melting at 95°. It dissolves in sulphuric acid forming a reddish-yellow solution, the coloration being probably due to the presence of the following compound.

*Difurfurylidenetriacetophenone*, $COPh\cdot CH[CH(C_4OH_3)\cdot CH_2\cdot COPh]_2$, like the corresponding benzaldehyde compound, exists in two isomeric modifications. When a mixture of an alcoholic solution of acetophenone and furfuraldehyde with aqueous soda and alcohol is allowed to remain at the ordinary temperature, the compound obtained crystallises out in white needles; it melts at 175°, and forms a brownish-red solution in sulphuric acid. If, on the other hand, the mixture be heated, the product crystallises in thin, quadratic prisms, melts at 211—212°, and yields a brown solution in sulphuric acid.

*Furfurylidenemethyl paratolyl ketone* forms yellow needles, melts at 67°, boils at 330°, and yields a yellow solution with sulphuric acid. *Furfurylidenedimethyl diparatolyl diketone*, $C_4OH_3\cdot CH(CH_2\cdot CO\cdot C_6H_4Me)_2$, crystallises in lustrous needles, melting at 112—113°, and yielding a yellow solution in sulphuric acid. A. H.

**4 : 5-Diphenyloctane-2 : 7-dione.** By CARL D. HARRIES and G. ESCHENBACH (*Ber.*, 1896, **29**, 2121—2127; compare this vol., i, 305). —Owing to the production of benzylacetone when benzylideneacetone is reduced, it seemed possible that the substance arising from diphenyl-4 : 5-octanedione-2 : 7 (*loc. cit.*) under the influence of sodium ethoxide, is due to the combination of that substance with unchanged benzylideneacetone; such a result would be analogous to the action of ethylic acetoacetate on benzylideneacetone (Abstr., 1894, i, 528), or the condensation of benzylideneacetone with benzylidenediacetone (this vol., i, 557). Attempts to produce the compound in question by the action of sodium ethoxide on a mixture of benzylacetone and benzylideneacetone, have, however, been unsuccessful, and this circumstance, taken in conjunction with the behaviour of the substance towards oxidising agents and bromine, appears to indicate that the original view of its formation is the correct one.

1 : 2-*Dimethyl*-4 : 5-*diphenylhexamethylene*,



$$\begin{array}{l}CHPh\cdot CH_2\cdot CHMe\\ \,| \qquad\qquad\quad\;\; |\\ CHPh\cdot CH_2\cdot CHMe\end{array},$$

is obtained by reducing diphenyl-4 : 5-octanedione-2 : 7 in alcoholic solution with zinc and hydrochloric acid; it crystallises from light petroleum in transparent crystals belonging to the triclinic system, and melts at 97°, boiling unchanged at 270°.

Diphenyl-4 : 5-octanedione-2 : 7 resists the action of gentle oxidising agents, yielding benzoic acid under more vigorous treatment. Concentrated nitric acid gives rise to a substance which melts indefinitely at 120—135°, and which the authors regard as a mixture of isomeric dinitrobenziles, $C_2O_2(C_6H_4\cdot NO_2)_2$. Bromine gives rise to hexabromodiphenyl-4 : 5-octanedione-2 : 7, stilbene dibromide, hexabromostilbene, tetrabromacetone, and pentabromacetone.

*Hexabromodiphenyl*-4 : 5-*octanedione*-2 : 7, crystallises from glacial acetic acid in small, white needles, and melts at 190—191°.

M. O. F.

**Dithienylphenylmethane and its Nitro-derivatives.** By Albert Töhl and A. Nahke (*Ber.*, 1896, **29**, 2205—2207).—*Dithienylphenylmethane*, $CHPh(C_4SH_3)_2$, is best prepared by the following method:—Thiophen (17 grams) and benzaldehyde (10 grams) are mixed with 50 grams of light petroleum and 20 grams of phosphoric anhydride, and the mixture left for several hours; after the reaction is over, water is added, and the whole is extracted several times with light petroleum; the extract is washed with alkali, dried, and fractionated. The crystalline fraction is dissolved in a little boiling alcohol, and ether added until drops of oil cease to be thrown down. The dithienylphenylmethane then crystallises in colourless needles, which melt at 74—75°. With isatin and sulphuric acid, it gives a brownish-red colour, which changes to green on warming. The same dithienylphenylmethane may be obtained by the following methods, the yield, however, is not good. (1) By heating a mixture of benzaldehyde and thiophen at 100° for several hours. (2) By heating a mixture of thiophen and benzaldehyde to boiling in the presence of zinc chloride. (3) By the action of sulphuric acid on a mixture of benzaldehyde and thiophen. (4) By the action of aluminium chloride on a mixture of benzylidene chloride and thiophen.

*Dithienylmetanitrophenylmethane*, obtained by the action of phosphoric anhydride on a solution of thiophen and metanitrobenzaldehyde in ether and chloroform, crystallises from light petroleum in plates which have a pearly lustre, melts at 72—73°, and is readily acted on by fuming nitric acid.

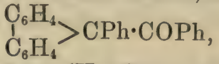
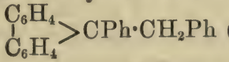
*Dithienylorthonitrophenylmethane* crystallises in needles and melts at 84°, and *dithienylparanitrophenylmethane* melts at 89—90°.

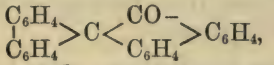
J. J. S.

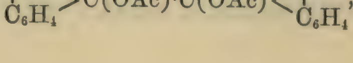
[**Coloured Rosaniline Bases.**] By Georg von Georgievics (*Ber.*, 1896, **29**, 2015—2016; compare this vol., i, 441).—The author has examined the precipitate, described by him as a coloured rosaniline base, for chlorine, and finds that no chlorine is present when it is purified by washing with water. The small amount of chlorine in the crude precipitate is due to sodium chloride, and not as Weil has suggested (this vol., i, 565) to a basic rosaniline hydrochloride.

A. H.

**Oxidation by means of Hydroxylamine Hydrochloride.** By Heinrich Biltz (*Ber.*, 1896, **29**, 2080—2082; compare E. von Meyer, Abstr., 1884, 1187; and Nietzki and Benckiser, Abstr., 1886, 450).—When triphenylvinylic alcohol (2 grams) is boiled with hydroxylamine hydrochloride ($3\frac{1}{2}$ grams) and absolute alcohol (30 grams) for 12 hours, it yields *phenylbenzoïn ethylic ether*. This is formed by the addition of the elements of alcohol, and the subsequent oxidation of the secondary alcoholic group thus formed. It crystallises in well developed rhombic crystals resembling those of barytes. It yields no derivatives with hydroxylamine, phenylhydrazine, semicarbazide, or aniline; this inactivity is probably due to stereochemical influences (compare Beckmann, *Annalen*, **252**, 74). That the reaction proceeds according to the equation $C_{20}H_{16}O + C_2H_5{\cdot}OH + NH_4OCl = C_{22}H_{20}O_2 + H_2O + NH_4Cl$, was proved by estimating the amount of ammonium chloride formed from a given weight of hydroxylamine hydrochloride. On hydrolysis with soda, the phenylbenzoïn ethylic ether is decomposed into benzoic acid and benzhydrol ethylic ether. J. J. S.

**Diphenyldiphenylenepinacolin and Tetraphenylenepinacolin.** By Heinrich Klinger and Carl Lonnes (*Ber.*, 1896, **29**, 2152—2156; compare this vol., i, 374; also Graebe and Stindt, this vol., i, 565).—*Diphenyldiphenylenepinacolin*,  $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>CPh\cdot COPh$, is obtained by oxidising diphenyldiphenylenethylene (Kaufmann, this vol., i, 242), and also from triphenylmethane, benzoic chloride, and potassium (compare Hanriot and St. Pierre, Abstr., 1889, 882). It separates from acetone in colourless, highly refractive crystals, and melts at 172°; the crystals are monoclinic, $a : b : c = 0\cdot7086 : 1 : 1\cdot2513$, $\beta = 59° 9' 40''$. The substance undergoes no change when heated with benzoic anhydride or acetic chloride at 150—160°, but yields benzoic acid and phenyldiphenylenemethane under the influence of phenylhydrazine or alcoholic potash. The *hydrocarbon*, $C_{26}H_{18}$, is obtained from diphenyldiphenylenepinacolin by the action of hot, fuming hydriodic acid, and crystallises in needles melting at 235°; oxidation converts it into the *compound*, $C_{26}H_{18}O_2$, which melts at 168°. Hanriot and St. Pierre obtained the same hydrocarbon, ascribing to it the formula $C_{26}H_{20}$; the hydrocarbon, $C_{26}H_{22}$, obtained by these investigators from potassium triphenylmethane and benzylic chloride, is regarded by the authors as *unsymmetrical diphenyldiphenylenethane*,  $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>CPh\cdot CH_2Ph$ (compare this vol., i, 375).

*Tetraphenylenepinacolin*,  $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>C<\genfrac{}{}{0pt}{}{CO-}{C_6H_4}>C_6H_4$, is obtained by treating an ethereal solution of fluorene ketone with acetic chloride and zinc dust, and is also produced on oxidising tetraphenylenethylene (compare Graebe and von Mantz, this vol., i, 442); it crystallises from benzene in colourless plates, melting at 258° (uncorr.), and is identical with bidiphenylenethylene oxide, obtained by Graebe and Stindt on heating the bromide of bidiphenylenethylene with water at 150° (this vol., i, 566). The authors advocate the foregoing expression for the constitution of tetraphenylenepinacolin in preference to the oxide formula already adopted (*loc. cit.*), owing to the properties of an *acid*, $C_{26}H_{18}O_2$, obtained by the action of alcoholic potash on the pinacolin. This substance, which melts at 243—244°, loses $H_2O$ when heated at 340°, tetraphenylenepinacolin being regenerated; it is readily oxidised in alkaline solution, yielding the *acid*, $C_{26}H_{18}O_3$, which melts at 177—179°, this substance giving rise to the *lactone*, $C_{26}H_{16}O_2$, which melts indefinitely at 213—219°. Hydriodic acid converts tetraphenylenepinacolin into the *hydrocarbon*, $C_{26}H_{16}$, which crystallises in white needles, and melts at 215°. Bromine is without action on tetraphenylenepinacolin, which, on oxidation, yields the compound $C_{26}H_{16}O_2$, melting at 269°.

*Tetraphenylenepinacone diacetate*,  $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>C(OAc)\cdot C(OAc)<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}$,

is produced along with tetraphenylenepinacolin and tetraphenylenethylene when an ethereal solution of fluorene ketone is treated with acetic chloride and zinc dust; it crystallises from a mixture of benzene and alcohol in rosettes of leaflets, and melts at 270°, evolving gas. The same compound has been obtained by Graebe and Stindt (this vol., i, 566). Hydrolysis with alcoholic potash gives rise to fluorene ketone and fluorene alcohol, whilst 70 per cent. sulphuric acid at 100° converts it into tetraphenylenepinacolin.

M. O. F.

**Diphenyldiphenylenethylene and Tetraphenylenethylene.** By Heinrich Klinger and Carl Lonnes (*Ber.*, 1896, **29**, 3157—3158).—It has been already mentioned (this vol., i, 375) that diphenyldiphenylenethylene, a colourless hydrocarbon, yields deep yellow solutions; the property is exhibited in an equal degree by the hydrocarbon remaining after fractional oxidation, and on crystallising the picrate fractionally, and regenerating the hydrocarbon from three separations, products were obtained which exhibited, in 1 per cent. benzene solution, a yellow colour comparable with that of a 0·075 per cent. solution of potassium chromate. The authors consequently attribute the property in question to the pure hydrocarbon, which they regard, from this point of view, as occupying an intermediate position between colourless tetraphenylethylene and red tetraphenylenethylene.

*Tetraphenylenethylene* is obtained as a bye-product in reducing fluorene ketone with acetic chloride and zinc dust; it is identical with bidiphenylenethylene, described by Graebe (Abstr., 1893, i, 38). It distils under diminished pressure without undergoing decomposition, and crystallises from benzene in beautiful red needles, which melt at 189—190° (uncorr.). M. O. F.

**γ-Amidonaphtholsulphonic acid.** By Ernst Täuber and Franz Walder (*Ber.*, 1896, **29**, 2267—2270).—γ-Amidonaphtholsulphonic acid is obtained by fusing 2-amidonaphthalene-3′:1′-disulphonic acid with alkalis (German Patent 53,076). It forms white, sparingly soluble needles, and reduces ammoniacal silver solutions and Fehling's solution. Nitrous acid converts it into the *diazo-sulphonic acid*, which is itself converted by alkalis into a deep blue colouring matter, having the same composition as the diazosulphonic acid. This is not affected by cold sulphuric acid, but decomposes when heated with it. The diazosulphonic acid readily yields the corresponding *hydrazine-sulphonic acid*, which crystallises in fascicular groups of colourless needles; these become red on exposure to light.

When this hydrazinesulphonic acid is boiled with copper sulphate, it is converted into a naphtholsulphonic acid, which, on treatment with sodium amalgam, yields α-naphthol. It follows from this that the original γ-amidonaphtholsulphonic acid is the 2-amido-1′-hydroxynaphthalene-3′-sulphonic acid. A. H.

**Isomeric Naphthalene Derivatives. IV. Diamidonaphthalenesulphonic acids.** By Paul Friedländer and W. H. Kiel-

BASINSKI (*Ber.*, 1896, **29**, 1978—1983).—The object of this research was to investigate the effect of the presence of the sulphonic group on the basicity of the naphthylenediamines. 1 : 2-Naphthylenediamine-4-sulphonic acid does not possess basic properties, and is less soluble in dilute hydrochloric acid than in water. 1 : 3′-Naphthylenediamine-4-sulphonic acid is prepared by the action of ammonia on 1 : 3′-amidonaphthol-4-sulphonic acid (German Patent, 77,157). The latter forms slender, sparingly soluble needles. It is converted by the action of sodium amalgam into 1 : 3′-amidonaphthol. 1 : 3′-Naphthylenediamine-4-sulphonic acid forms sparingly soluble needles, and acts as a monacid base, the *platinochloride*, $[C_{10}H_5(NH_2)_2 \cdot SO_3H]_2,H_2PtCl_6$, crystallising in yellow prisms. The *ammonium salt* crystallises in nacreous plates, whilst the *sodium salt* is less soluble, and forms tablets.

1 : 3′-*Naphthylenediamine*-4 : 1′-*disulphonic acid* is obtained by the reduction of the corresponding nitro-compound (Kalle & Co., German Patent, 72,665). When its tetrazo-derivative is boiled with cuprous chloride, it yields the *monosodium salt of* 1 : 3′-*dichloronaphthalene*-4 : 1′-*disulphonic acid*, which crystallises in yellowish needles, the *normal silver salt* crystallising in slender, readily soluble needles. The acid is converted by distillation with dilute sulphuric acid into 1 : 3′-dichloronaphthalene. Sodium amalgam, moreover, converts the naphthylenediaminedisulphonic acid into 1 : 3′-naphthylenediamine.

1 : 3′-Naphthylenediamine-4 : 1′-disulphonic acid crystallises in sparingly soluble needles, and does not possess basic properties, the introduction of the second sulphonic group into the ring, which only contained an amido-group in the acid last described, having thus destroyed the basic properties which were shown by that acid. 1 : 3′-*Naphthylenediamine*-3 : 1′-*disulphonic acid* is formed along with the foregoing acid, but can be separated from it by the different solubility of its sodium salt; its constitution was determined in the same way as that of its isomeride. The dichloronaphthalenedisulphonic acid yields a readily soluble monosodium salt and a less soluble normal salt. The acid has no basic properties. 1 : 4′-Naphthylenediamine-2-sulphonic acid (L. Cassella & Co., German Patent, 70,890) is sparingly soluble in water, whilst the ammonium and sodium salts are readily soluble; this acid has well marked basic properties, and yields a crystalline, sparingly soluble *hydrochloride*, and an almost insoluble *sulphate*. A. H.

**New Method for Hydroxylating in the Anthraquinone Series.** By LEONHARD WACKER (*J. pr. Chem.*, 1896, [2], **54**, 88—94).—Anthraquinone and hydroxyanthraquinones may be hydroxylated by treatment with persulphates in sulphuric acid solution. The higher hydroxylated compounds are obtained by this method in the form of their sulphates, characterised by their solubility in water and their conversion into polyhydroxyanthraquinones when heated with sufficiently concentrated sulphuric acid. The formation of the higher hydroxylated compounds is conditioned by the ability of the sulphuric acid to act as a substituting agent; thus, if acid of 66° B. is used, or a feebly fuming acid, at low temperatures, lower hydroxylated dyes are exclusively formed, however much persulphate is used.

The paper contains details of proportions to be employed in particular cases, most of which have appeared in patent specifications. The following table gives a general view of the kind of results obtained.

| Raw material. | Conditions of working. | | | |
|---|---|---|---|---|
| | Sulphuric acid of 66° B., and about 2 parts of persulphate. | In feebly fuming sulphuric acid. | | |
| | | At 20—50°, with 1—2 parts of persulphate. | At 80—150°. | |
| | | | With 2 parts of persulphate. | With 4 parts and upwards of persulphate. |
| Anthraquinone .. | Monohydroxyanthraquinone | Partial action with formation of cyanin | Partial action with formation of cyanin | Cyanin. |
| Alizarin ........ | No apparent action | Purpurin...... | more violet dye | Cyanin. |
| Anthrapurpurin.. | Hydroxyanthrapurpurin | Hydroxyanthrapurpurin | more violet dye | Cyanin. |
| Flavopurpurin ... | Hydroxyflavopurpurin | Hydroxyflavopurpurin | more violet dye | Cyanin. |
| Anthrachrysone.. | — | — | — | Cyanin. |

Ammonium persulphate is generally used.

The conversion of β-hydroxyanthraquinone into quinizarin by this method is of theoretical interest as involving a migration of a hydroxyl group. A. G. B.

**Crystallographic Properties of Alkylcamphors of the Aromatic Series.** By JULES MINGUIN (*Compt. rend.*, 1896, **123**, 248—249).—*Benzylcamphor* forms rhombic prisms of 99·05°. For $b = 1000$, $h = 857$. The only modification is $a^1$, which is developed to such an extent as to extinguish $p$.

*Anisylcamphor* forms prisms of 105° 45′ in which $b = 1000$, $h = 675·1$, the faces commonly observed being $m, g^1, g^3, a^1, e^1, b^{\frac{1}{2}}$, the domes and the faces $g^3$ being, as a rule, highly developed.

*Methylsaligenylcamphor*, isomeric with anisylcamphor, does not crystallise distinctly, but seems to belong to the rhombic system.

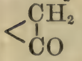
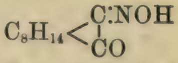
*Ethylsaligenylcamphor* forms rhombic prisms with an angle of 110°; $b = 1000$, $h = 222·9$. The faces observed are $m, g, g^3, h^1, e^{\frac{1}{2}}, a^1$, but the faces $a^1$ are often wanting, owing to the development of the faces $e^{\frac{1}{2}}$.

In no case were hemihedral faces observed. The crystalline similitude previously referred to is also observed in the reduction derivatives, and an angle of about 160° corresponding with a face $g^3$ is found in the zone $mm^1$, and this is connected with the observed constancy of the angle of the prism. The same angle of 160° occurs in the bromine derivatives obtained from benzylidene and the benzylcamphors. Further, the products of reduction are all rhombic, even when the original compound is monoclinic, and the two atoms of hydrogen seem to have a special influence in modifying the domes in such a manner as to increase the symmetry. C. H. B.

**Camphoric Mononitrile, its Anhydride and Anilide.** By Albin Haller and Jules Minguin (*Compt. rend.*, 1896, **123**, 216—220).—By the action of acetic chloride on camphoroxime, the authors have obtained a compound, $C_{20}H_{28}N_2O_3$, and an acid, $C_{10}H_{15}NO_2$, which in all probability are identical with the compounds obtained by Oddo and Leonardi (*Gazzetta*, **26**, i, 405) in the same way from a camphoroxime prepared in a somewhat different manner.

The acid $C_{10}H_{15}NO_2$ is converted into camphoric acid and ammonia when treated with concentrated aqueous potash, and hence must be regarded as camphoric mononitrile. The compound $C_{20}H_{28}N_2O_3$ is the anhydride of this acid, into which it is converted by the action of alcoholic potash, and from which it can be obtained by heating with a molecular proportion of phenylic isocyanate below 100°, the other products being carbonic anhydride and diphenylcarbamide. If the mixture of anhydride and diphenylcarbamide thus produced is heated above 160°, there is a further evolution of carbonic anhydride, and the anilide of camphoric mononitrile, $CN\cdot C_8H_{14}\cdot CO\cdot NHPh$, is produced.

The specific rotatory powers of the mononitrile, anhydride, and anilide are +67·70, +54·66, and +62·6 respectively, and their melting points are 149—150°, 175—176°, and 197°.

The formation of camphoric mononitrile from camphoroxime may be explained by assuming that the NOH group has the same influence as any other negative radicle introduced into the methylene of the  $<\begin{matrix}CH_2\\|\\CO\end{matrix}$ group, and renders the union between the methylene and the carbonyl groups very unstable, with the result that  $C_8H_{14}<\begin{matrix}C{:}NOH\\|\\CO\end{matrix}$ becomes $CN\cdot C_8H_{14}\cdot COOH$. The anhydride is a secondary product of the action of the excess of acetic chloride on the acid. This view is supported by the facts that cyanocamphor is readily converted into cyanocampholic acid, and that the latter yields an anhydride when heated with phenylic isocyanate. C. H. B.

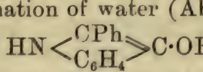
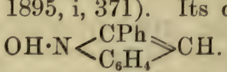
**Camphoric acid. III.** By William A. Noyes (*Ber.*, 1896, **29**, 2326—2328; compare Abstr., 1895, i, 295 and 552).—According to Tiemann's formula for camphoric acid (Abstr., 1895, i, 428), the carboxylic group in amidodihydrocampholytic and amidolauronic acids should be secondary, and the same velocity of etherification would be then exhibited by both acids; it is found, however, that the action of boiling alcohol in presence of sulphuric acid converts into ethylic salt 10 times as much of the former acid as of the latter, and it therefore appears that amidodihydrocampholytic acid contains a secondary carboxylic group, whilst in amidolauronic acid this complex is tertiary.

*Hydroxylauronic acid*, $OH{\cdot}C_8H_{14}{\cdot}COOH$, is obtained from ethylic amidolauronate by the action of nitrous acid, ethylic isolauronate (Walker's allocampholytic acid) being also formed; it is a viscous liquid, and dissolves with some difficulty in water. The *copper* salt is a bright green powder, which dissolves sparingly in water; it contains $1H_2O$. Chromic acid oxidises hydroxylauronic acid in the cold, producing a ketone and carbonic anhydride; it appears probable, therefore, that the substance in question is a $\beta$-hydroxy-acid, the hydroxyl group corresponding with the amido-group in amidolauronic acid, and one of the carboxylic groups in camphoric acid, which the author regards as a derivative of succinic acid.

Fresh evidence in favour of the view that *cis*-campholytic acid (Abstr., 1895, 552) is an $\alpha\beta$-unsaturated acid, is afforded by converting it into dihydro-*cis*-campholytic acid by means of amylic alcohol and sodium, and treating with alcoholic potash the $\alpha$-bromodihydro-*cis*-campholytic acid obtained from it, when *cis*-campholytic acid is regenerated quantitatively.

The amide of dihydro-*cis*-campholytic acid is converted by sodium hypobromite into an *amine*, $C_8H_{15}{\cdot}NH_2$, which boils at 156·5°, and has the sp. gr. 0·8431 at 20°/20°. Nitrous acid converts this base into the *hydrocarbon*, $C_8H_{14}$, and the secondary *alcohol*, $C_8H_{15}{\cdot}OH$; the latter is oxidised by chromic acid to a *ketone*, the *oxime* of which crystallises from alcohol in needles or prisms, and melts at 112—113°. According to Kipping, the melting point of dimethyl-1:3-cyclohexanone-2 is 114—115°, whilst Zelinsky describes this substance as melting at 104—105°; the author has prepared it by another method in a form melting at 120—122°, and it is therefore uncertain whether this substance is identical with the foregoing oxime. M. O. F.

**Vicin, a Glucoside.** By C. HEINRICH L. RITTHAUSEN (*Ber.*, 1896, **29**, 2108—2109).—Although vicin is described as an alkaloïd in Beilstein's Handbook, the author has shown that this substance is a glucoside. Hydrolysis with dilute sulphuric acid gives rise to divicin and a mixture of glucose and galactose. M. O. F.

**Hydroxy-2′-phenylindole and Nitrosobenzoic acid.** By EMIL FISCHER (*Ber.*, 1896, **29**, 2062—2064).—The name hydroxy-2′-phenylindole has been substituted for phenylindoxyl, the name previously given to the substance obtained from benzoïnoxime by the elimination of water (Abstr., 1895, i, 371). Its constitution must be either  $HN<\begin{matrix}CPh\\C_6H_4\end{matrix}>C{\cdot}OH$ or  $OH{\cdot}N<\begin{matrix}CPh\\C_6H_4\end{matrix}>CH$. On oxidation with dilute potassium permanganate in the cold, it yields orthonitrosobenzoic acid and benzoylanthranilic acid. No definite conclusions as to the constitution of the hydroxyindole can be drawn from these products of oxidation.

*Orthonitrosobenzoic acid* is best separated from benzoylanthranilic acid as follows: The mixture of the two is dissolved in ammonia, the benzoylanthranilic acid is precipitated by acidifying, and the mother liquor is then extracted some 10 times with ether. The ethereal solution, on concentration, yields the nitroso-acid, whilst a considerable quantity of benzoic acid still remains in solution. After recrystallisation from boiling absolute alcohol, orthonitrosobenzoic acid forms almost colourless crystals, but it turns brown above 180°, and is completely decomposed at about 210°. The acid is extremely sparingly soluble in cold alcohol and ether, but more readily in hot alcohol and in glacial acetic acid, yielding green solutions. The ammoniacal solution is also coloured green. It is readily reduced to anthranilic acid by dissolving in ammonia, then saturating the solution with hydrogen sulphide, and finally heating at 100° for an hour in sealed tubes. J. J. S.

**Alkyloxides of 1-Hydroxyquinoline.** By ADOLPH CLAUS and EMIL MOHL (*J. pr. Chem.*, 1896, **54**, 1—17).—1-*Hydroxyquinoline methosulphate*, $(C_9NH_6{\cdot}OH)_2,Me_2SO_4 + 3H_2O$, is prepared by heating an aqueous alcoholic solution of the methiodide with the calculated quantity of silver sulphate in a reflux apparatus; it crystallises from the concentrated filtrate in large, lustrous, golden-yellow prisms, melts at 226°, and dissolves freely in water, but more sparingly in alcohol. As has been indicated already (Abstr., 1892, 877), it is not possible to produce from this methosulphate an "intermediate product" such as is obtainable from the methiodide by treatment with alkalis (Abstr., 1890, 1323); however small a proportion of alkali is used, an equivalent proportion of the methosulphate is converted into the methohydroxide, the rest remaining unchanged.

1-*Hydroxyquinoline methodichromate*, $(C_9NH_6{\cdot}OH)_2,Me_2Cr_2O_7 + 2H_2O$, is precipitated in the form of dark yellow, small, lustrous needles when potassium dichromate is added to a solution of the methiodide; it is sparingly soluble in alcohol and water, and decomposes at 80°. The *methoxalate*, $(C_9NH_6{\cdot}OH)_2,Me_2C_2O_4 + H_2O$, prepared by neutralising a solution of the methohydroxide, evaporating to dryness, dissolving in absolute alcohol, and adding ether, forms dark yellow, lustrous, slender crystals; it melts at 151°, and dissolves freely in water, but more sparingly in alcohol. Neither of these two salts yields an "intermediate product," and this seems to be generally the case with the salts of oxy-acids.

1-Hydroxyquinoline ethobromide crystallises with $1\frac{1}{2}H_2O$, not $2\frac{1}{2}$ (Abstr., 1893, i, 484), and the crystals melt at 72°. The benzochloride (*loc. cit.*) crystallises with $1\frac{1}{2}H_2O$.

4 : 1-*Bromhydroxyquinoline methiodide*, prepared by heating its components (Abstr., 1892, 354) for 6—8 hours in a sealed tube at 130—135°, crystallises in golden-yellow, lustrous laminæ, with $1H_2O$, and melts at 157°. By treatment with half an equivalent of an alkali, it yields the "*intermediate product*,"

$$HO{\cdot}C_9NH_5BrMe{\cdot}O{\cdot}C_9NH_5BrMeI,$$

in the form of small, brilliant, blood-red crystals, which melt at 182°. The *methohydroxide*, which is formed when excess of alkali is used, crystallises in large, lustrous, brownish-red prisms, and melts at 180°.

Besides the two methods by which 1-methoxyquinoline methiodide has been prepared (Abstr., 1890, 1323), a third is available, namely, the action of methylic iodide on the inner anhydride of 1-hydroxyquinoline methohydroxide; this compound, $C_9NH_6MeO$ [$O = 1 : 1'$], was prepared by heating the methohydroxide (which crystallises with $2H_2O$, not $1H_2O$; Abstr., 1892, 877) at 70—80° in a current of air. All three methods yield the same compound.

1-*Ethoxyquinoline methiodide* is prepared in the usual way from its components, but cooling is essential; it crystallises in thick, transparent, bright yellow prisms, melts at 200°, and is soluble in hot water or alcohol. When treated with silver chloride, the corresponding *methochloride* is obtained; this crystallises in nearly colourless, lustrous prisms and needles with $2H_2O$, and melts at 107°. When the methiodide is treated with alkalis, it yields a base, which is soluble in ether, and is probably the corresponding alkylenequinolinium base (compare Abstr., *loc. cit.*); in this respect, the 1-alkyloxyquinoline alkyl haloïd salts resemble the 3-derivatives. With silver oxide, however, the resemblance between the 1- and the 3-derivatives is not maintained; when an aqueous solution of 3-ethoxyquinoline methochloride is shaken with ether and silver oxide, the methohydroxide is formed and remains dissolved in the water; similar treatment of an aqueous solution of 1-ethoxyquinoline methochloride produces the base, which is soluble in ether, so that the water retains none. A. G. B.

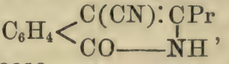
**Reduction Products from Cinchomeronic acid and from Apophyllenic acid.** By Wilhelm Koenigs and Fritz Wolff (*Ber.*, 1896, **29**, 2187—2192; compare this vol., i, 251).—When methylic cinchomeronate is reduced with sodium and alcohol, it yields an ethereal salt of hexahydrocinchomeronic acid. The reduced mixture is best hydrolysed by repeated evaporation to dryness with dilute hydrochloric acid, and the hydro-acid separated from the unaltered acid by conversion into its nitrosamine; the latter may then be extracted with ether and converted into the acid.

The *hydrochloride* of the hexahydro-acid crystallises in anhydrous forms, melts at 237°, is readily soluble in cold water, and sparingly in cold alcohol. Its *aurochloride* melts at 205°, and on boiling in aqueous solution readily decomposes and yields metallic gold.

*Hexahydrocinchomeronic acid* melts at 256°, and is readily soluble in water. It is a monobasic acid, but its nitrosamine is dibasic. Its *calcium* salt crystallises with $5H_2O$, and is readily soluble in water. The *nitrosamine* is an oil, and yields a readily soluble *barium* salt, a gelatinous *silver* salt, and a crystalline *strychnine* salt. The hexahydro-acid is not acted on when boiled with a solution of sodium in amylic alcohol (compare Besthorn, this vol., i, 252).

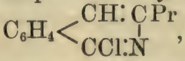
Apophyllenic acid (methylbetaïncinchomeronic acid; Vongerichten, Abstr., 1880, 110) is best obtained from cotarnine (Roser, *Annalen*, **254**, 354). This is first heated with phosphorus pentachloride at 160—170°, then treated with ice, and, after boiling with water, filtered; the filtrate is evaporated to dryness, and the tarry residue oxidised with a mixture of concentrated nitric acid and water. Apophyllenic acid, when reduced with tin and concentrated hydrochloric acid, yields n-*methylhexahydrocinchomeronic acid;* this is best purified by conversion into its ethylic salt, which can be extracted with ether. The acid, which crystallises slowly from its concentrated aqueous solutions, can also be precipitated by adding alcohol. It melts and decomposes at 206—207°. J. J. S.

**Synthesis of 3′-Propylisoquinoline.** By JACQUES M. ALBAHARY (*Ber.*, 1896, **29**, 2391—2398).—The synthesis was effected by the method introduced by Gabriel and Neumann (Abstr., 1892, i, 228). *ψ-Dibutyrylorthocyanobenzylic cyanide*, $CN{\cdot}C_6H_4{\cdot}C(CN)\colon CPr{\cdot}O{\cdot}COPr$, obtained by heating orthocyanobenzylic cyanide with butyric anhydride and sodium butyrate, crystallises in slender, matted needles, melting at 105°. When it is heated with alcoholic potash, it yields 4′ : 3′-*cyanopropylisocarbostyril*,



$C_6H_4<\begin{array}{l}C(CN)\colon CPr\\ CO\text{——}NH\end{array}$

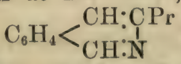
, which crystallises in slender needles melting at 221°. A small amount of a substance which melts at 80°, and has the composition $C_{15}H_{16}N_2O$, is also formed. Cyanopropylisocarbostyril is readily converted by boiling with sulphuric acid and water into *propylisocarbostyril*, which crystallises in yellowish needles, melting at 130—131°. When this substance is heated with phosphorus oxychloride, it yields 1′ : 3′-*chloropropylisoquinoline*,



$C_6H_4<\begin{array}{l}CH\colon CPr\\ CCl\colon N\end{array}$

, which is a yellow liquid, boiling at 302—303° (pressure = 746 mm.). It has a characteristic odour, and is only a weak base. The *platinochloride* melts and decomposes at 195°, and the *aurochloride* melts at 140—141°. The halogen atom readily reacts with the sodium salts of compounds of alcohols and phenols. 1′ : 3′-*Methoxypropylisoquinoline* is a yellowish oil, which boils at 281°. The *picrate* melts at 130—134°; the *platinochloride* melts and decomposes at 169—170°, and the *aurochloride* at 130—132°. The *chromate* is a thick, reddish-brown oil. 1′ : 3′-*Ethoxypropylisoquinoline* boils at 287°; the *picrate* melts at 130°, and the *platinochloride* decomposes at 178—182°. 1′ : 3′-*Phenoxypropylisoquinoline* is an unstable oil, which has not been obtained pure. The *picrate* melts at 96—98°.

Chloropropylisoquinoline is reduced by hydriodic acid and phosphorus at 160—170°, and is thus converted into 3′-*propylisoquinoline*,



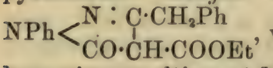
$C_6H_4<\begin{array}{l}CH\colon CPr\\ CH\colon N\end{array}$

; this has a characteristic pleasant odour, boils at 271°, and has the sp. gr. 1·01561 at 24°. The *picrate* melts at 161°; the *aurichloride* melts and decomposes at 118°; whilst the *platinochloride* decomposes at 189° without melting. A. H.

**Correction [Pyrazolone Derivatives].** By WILHELM AUTENRIETH (*Ber.*, 1896, **29**, 2169—2171).—The author points out that the azo-compound melting at 155°, obtained by the action of ethylic β-chlorocrotonate on phenylhydrazine (this vol., i, 627), is identical with Knorr's phenylhydrazone of phenylmethyl-4-ketopyrazolone (Abstr., 1888, 724).

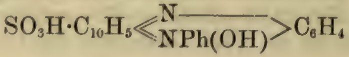
The dibenzoyl derivative of bisphenylmethylpyrazolone (this vol., i, 627) is identical with Nef's benzoyl derivative of bis-1 : 2 : 3-phenylbenzoylmethylpyrazolone (Abstr., 1892, 146). Although previously described by the author as melting at 189—190°, a re-examination shows that its melting point is 194—196°; Nef states that the substance melts at 203°. M. O. F.

**Ethylic Mono- and Di-phenacetylmalonate, and the Action of Phenylhydrazine on Ethereal Salts of Acidyl Derivatives of Malonic acid.** By Heinrich Schott (*Ber.*, 1896, **29**, 1985—1996).—Phenacetic chloride reacts with ethylic sodiomalonate, free from alcohol, to form a mixture of the mono- and di-derivatives. *Ethylic phenacetylmalonate* is a colourless liquid which dissolves readily in aqueous soda, and in aqueous solution gives a red coloration with ferric chloride. *Ethylic diphenacetylmalonate* is insoluble in dilute soda, and in alcoholic solution gives no coloration at first with ferric chloride, although a coloration is produced when the solution is allowed to remain, the monophenacetyl derivative being formed. These two substances are accompanied by a third of unknown constitution, which is only formed in small quantity, has the formula $C_{12}H_{10}O_3$, and melts at 114—117°.

Phenylhydrazine reacts with ethylic phenacetylmalonate in two ways. One portion is decomposed with formation of phenacetylphenylhydrazide and ethylic malonate, whilst the other forms a pyrazolone. *Ethylic* 1 : 3 : 5-*phenylbenzylpyrazolone*-4-*carboxylate*,  $NPh\Big<\begin{array}{l}N : C\cdot CH_2Ph\\ CO\cdot CH\cdot COOEt\end{array}$, which is thus produced, crystallises in colourless prisms melting at 124—127°. Ferric chloride produces a deep violet coloration. The same products are formed from ethylic diphenacetylmalonate, one of the phenacetyl groups being first eliminated as phenacetylphenylhydrazide.

Ethylic acetylmalonate yields with phenylhydrazine an unstable compound melting at about 80°, which has not been obtained pure, but is probably the hydrazone. No acetylphenylhydrazide is formed. Ethylic diacetylmalonate, on the other hand, yields β-acetylphenylhydrazide and *ethylic* 1 : 3 : 5-*phenylmethylpyrazolone*-4-*carboxylate*, which forms a crystalline powder, and melts at 119—121·5°. It is probably this substance which was described by Michael as the hydrazone (Abstr., 1888, 1054). A. H.

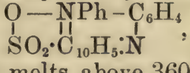
**Azonium Compounds from β-Naphthaquinonesulphonic acid and Phenylorthophenylenediamine.** By Friedrich Kehrmann and E. Locher (*Ber.*, 1896, **29**, 2072—2075).—Böniger's 1 : 2-naphthaquinone-4-sulphonic acid readily reacts in dilute acid solutions with phenylorthophenylenediamine to form the two isomeric azonium compounds



$$SO_3H\cdot C_{10}H_5\ll\begin{array}{l}N\text{————}\\ NPh(OH)\end{array}\!\!>C_6H_4$$

[$N:NPh\cdot OH:SO_3H = 1:2:4$ and $2:1:4$], the latter, however, being only obtained as its inner anhydride; they are best separated by fractional crystallisation from acetic acid.

The first compound crystallises in brownish-yellow, glistening crystals, and melts at 302—304°; it is only very sparingly soluble in water, but more readily in dilute alcohol and acetic acid. The solutions are bright yellow and exhibit a yellowish-green fluorescence. A trace of aniline colours the alcoholic solution magenta, owing to the formation of phenylrosinduline. With alkalis, it yields rosindone; with hydroxylamine and phenylhydrazine, it yields the rosindone oxime and hydrazone respectively.

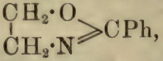
The second compound,  $\begin{array}{l} O\text{—}NPh-C_6H_4 \\ | \quad\;\; \| \qquad\quad | \\ SO_2\cdot C_{10}H_5:N \end{array}$, crystallises in glistening, reddish-brown prisms, and melts above 360°. It is sparingly soluble in water, moderately in alcohol, and readily in 70 per cent. acetic acid. Its solutions have a reddish-yellow colour and do not fluoresce. Characteristic is its intensely sweet taste; it dissolves in sulphuric acid yielding a dirty purple-red solution. J. J. S.

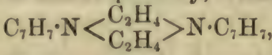
**Naphthazines.** By OTTO FISCHER and ROB. ALBERT (*Ber.*, 1896, **29**, 2086—2091; compare Fischer and Junk, Abstr., 1893, i, 283).—The naphthazine (m. p. 296°) previously described is now stated to be *β-naphthalido-sym.-naphthazine*, $C_{10}H_7\cdot NH\cdot C_{10}H_5{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_{10}H_6$, [$N:N:NH = 1:2:4$; $N:N = 1:2$], since, when heated with acetic and hydrochloric acids at high temperatures, it is decomposed into β-naphthylamine and a hydroxynaphthazine, which, on distillation with zinc dust, yields sym-αβ-naphthazine, melting at 242° (Matthes, Abstr., 1890, 993). The same naphthalidonaphthazine may also be obtained by the action of β-naphthylamine on β-amidonaphthazine. It is best purified by first washing with boiling alcohol and then crystallising from nitrobenzene. The hydrochloride, obtained by heating a xylene solution of the base with an alcoholic solution of hydrogen chloride, forms yellowish-red crystals.

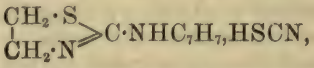
*αββ-Naphthazine*, obtained by the action of ββ-naphthalenediamine in cold acetic acid solution on β-naphthaquinone, crystallises in small, yellowish-brown needles. It melts at 240°, and gives a reddish-violet solution with concentrated sulphuric acid. It differs from sym-naphthazine in showing a yellowish-green fluorescence in dilute benzene solution. Its acetic acid solution is not fluorescent.

*α-Amido-sym-naphthazine* is obtained, together with Witt's unsym-αβ-naphthazine by the elimination of water and ammonia from nitroso-β-naphthylamine and α-naphthylamine. The best yield of the sym. compound is obtained by working at as low a temperature as possible. It crystallises in light yellow needles which have a green lustre, melts at 325°, and sublimes at higher temperatures. It is practically insoluble in benzene and in alcohol, but gives a yellowish-green fluorescence to the solvents. The salts with mineral acids are red. When heated with concentrated hydrochloric acid, the sym. naphthazine is decomposed into ammonia and the hydroxynaphthazine described above. J. J. S.

**Substituted Hydroxyphenyltriazoles.** By GEORGE YOUNG (*Ber.*, 1896, **29**, 2311—2312).—The author points out that 3 : 1 : 5-hydroxydiphenyltriazole, recently obtained by Widman (Abstr., 1896, i, 629), has been already described by him (Trans., 1895, 1064). According to his observations, all aromatic substituted hydroxyphenyltriazoles, which contain no amido-group, are, contrary to the statement of Widman, insoluble in dilute acids; they dissolve in warm concentrated hydrochloric acid, and are precipitated unchanged on the addition of water. M. O. F.

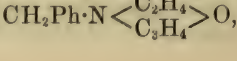
**Hydroxyl and Halogen Derivatives of Secondary and Tertiary Bases.** By SIEGMUND GABRIEL and ROBERT STELZNER (*Ber.*, 1896, **29**, 2381—2391).—$\mu$-Phenyloxazoline,  $\begin{matrix}CH_2\cdot O \\ | \\ CH_2\cdot N\end{matrix}\!\!>\!CPh$, is readily converted by reduction with sodium and boiling amylic alcohol into *benzylhydroxyethylamine*, $CH_2Ph\cdot NH\cdot CH_2\cdot CH_2\cdot OH$, which is a thick, almost odourless oil, and boils with partial decomposition at about 280°. It dissolves readily in water, forming a strongly alkaline solution. The *aurochloride* forms pointed, rhombic tablets, melting at 105°. The *picrate* melts at 135—136°. The *nitrosamine* is an oil. Concentrated hydrochloric acid at 170° converts the base into benzylchlorethylamine hydrochloride (Goldschmiedt and Jahoda, Abstr., 1891, 1351), the *platinochloride* of which melts and decomposes at 180—181°.

*Benzylbromethylamine* crystallises in long, slender needles, melting at 190—191°. The corresponding *picrate* melts at 147°. When a solution of benzylbromethylamine hydrobromide is distilled with an alkali, *benzylvinylamine*, $C_7H_7\cdot NH\cdot C_2H_3$, which is a colourless oil, passes over in small quantity, whilst a crystalline mass of *dibenzylpiperazine*,  $C_7H_7\cdot N\!<\!\begin{matrix}C_2H_4 \\ C_2H_4\end{matrix}\!>\!N\cdot C_7H_7$, remains behind in the flask. This substance forms pointed rhombic crystals, melts at 92°, and can also be obtained by the action of benzylic chloride on piperazine; the *hydrochloride* is sparingly soluble, and crystallises in plates. n-*Benzylethylene-ψ-thiocarbamide thiocyanate*,



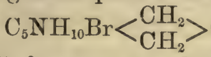
$$\begin{matrix}CH_2\cdot S \\ | \\ CH_2\cdot N\end{matrix}\!\!>\!C\cdot NHC_7H_7,HSCN,$$

is formed by the action of potassium thiocyanate on the hydrobromide of the bromo-base; it crystallises in needles melting at 165—166°.

Benzylhydroxyethylamine may also be prepared by the action of benzylamine on ethylene oxide. It is then accompanied by *benzyldihydroxydiethylamine*, $CH_2Ph\cdot N(C_2H_4\cdot OH)_2$, which is a colourless oil, and boils at 225—225·5° (pressure = 40 mm.). It is converted by hydrobromic acid into *benzyldibromodiethylamine hydrobromide*, which crystallises in short prisms, and melts at 191°. The free *base* is an oil, and the corresponding *picrate* melts at 138—139°. The filtrate from this bromo-base contains *benzylmorpholine hydrobromide*, which crystallises in colourless plates, melting at 234—235°. The free base, *benzylmorpholine*,  $CH_2Ph\cdot N\!<\!\begin{matrix}C_2H_4 \\ C_3H_4\end{matrix}\!>\!O$, is a colourless oil, which has a faint odour of benzylamine, and boils at 260—261°. The *hydrochloride* decomposes at 244—245°, the *platinochloride* at 211°. The *picrate* melts at 184—185°, whilst the *aurochloride* melts and decomposes at 202—203°. A chloride and platinochloride of a base, probably identical with the above, have been described by Goldschmiedt and Jahoda, who, however, have given lower melting points for these compounds.

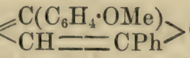
1-γ-*Phenoxypropylpiperidine*, $C_5NH_{10}\cdot C_3H_6\cdot OPh$, is prepared by heating piperidine with phenylic γ-chloropropylic ether. It is an oil, which boils at 313°, and yields a crystalline *hydrochloride* and a *picrate* which melts at 113°. Attempts to displace the phenoxy-group by chlorine failed, but the compound reacts with hydrobromic acid at 100° to form 1-γ-*bromopropylpiperidine hydrobromide*,

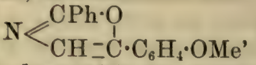
$$C_5NH_{10}C_3H_6Br,HBr,$$

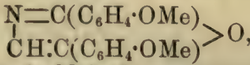
which crystallises in long, flat needles, melting at 212° (compare Laun, *Ber.*, **17**, 680). The *picrate* melts at 116—117°. When the base is set free and heated, only a very small amount of it distils over, the greater portion being converted into *trimethylenepiperylium bromide*,  $C_5NH_{10}Br{<}{\scriptstyle\begin{matrix}CH_2\\CH_2\end{matrix}}{>}CH_2$, which is not decomposed by aqueous alkalis; it forms a very hygroscopic, crystalline mass. The *picrate* melts at 239—240°, and is obtained by the direct action of picric acid. The bromide is decomposed by silver oxide, and the hydroxide thus formed yields with hydrochloric acid and platinic chloride the *platinochloride*, which melts at 185—187°. The *aurochloride* melts at 220°. When the hydroxide is treated with an excess of hydrobromic acid, it is reconverted into the original bromopropylpiperidine hydrobromide. An excess of hydrochloric acid converts it into the corresponding 1-γ-*chloropropylpiperidine hydrochloride*, which crystallises in colourless scales, and melts and decomposes at 220°.

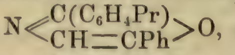
A. H.

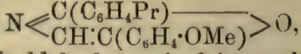
**Aromatic Oxazoles and Imidazoles.** By STEPHAN S. MINOVICI (*Ber.*, 1896, **29**, 2097—2106; compare this vol., i, 262.)—According to the observation of E. Fischer (*loc. cit.*), β : μ-diphenyloxazole is produced by condensation of benzaldehydecyanhydrin with benzaldehyde, and the author, applying this principle to numerous aromatic aldehydes and cyanhydrins, has found that in general, action takes place in a normal way, whilst in two cases, the compound produced by the action of the aldehyde on an amide arising from the nitrile is also formed.

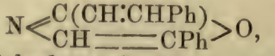
β-*Phenyl*-μ-*methoxyphenyloxazole*,  $N{<}{\scriptstyle\begin{matrix}C(C_6H_4\cdot OMe)\\CH=\!=CPh\end{matrix}}{>}O$, is produced when hydrogen chloride is led into an ice-cold, ethereal solution of anisaldehyde and benzaldehydecyanhydrin, the *hydrochloride* crystallising from the liquid in colourless needles or prisms, which melt and evolve hydrogen chloride at 173—174°; the base, which melts at 99°, and boils above 360°, is obtained by adding water to an alcoholic solution of the hydrochloride. The *picrate* decomposes and melts at 195°; the *sulphate* and *nitrate* melt at 225° and 116°, respectively. *Methoxybenzylidenemandelamide*, $OMe\cdot C_6H_4\cdot CH\vdots N\cdot CO\cdot CHPh\cdot OH$, is deposited on evaporating the ethereal mother liquor of the foregoing substance; it melts at 182°, and, when heated at 180° with dilute alcohol, yields ammonia, anisaldehyde, and mandelic acid.

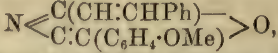
*μ-Phenyl-β-methoxyphenyloxazole*,  $\mathrm{N}{<}\begin{array}{l}\mathrm{CPh{\cdot}O}\\ \mathrm{CH{=}C{\cdot}C_6H_4{\cdot}OMe}\end{array}$, is obtained from anisaldehydecyanhydrin and benzaldehyde, methoxymandelamide being produced at the same time; it crystallises from ether in slender needles melting at 84—85°, and the *hydrochloride* evolves hydrogen chloride and melts at 195°. *Benzylidenemethoxymandelamide*, $\mathrm{CHPh{:}N{\cdot}CO{\cdot}CH(OH){\cdot}C_6H_4{\cdot}OMe}$, is another bye-product; it melts at 183°, and, when heated at 180° with dilute alcohol, yields ammonia and benzaldehyde, along with an acid which sublimes at 230° without undergoing fusion.

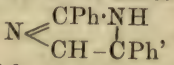
*β : μ-Dimethoxydiphenyloxazole*,  $\begin{array}{l}\mathrm{N{=}C(C_6H_4{\cdot}OMe)}\\ \mathrm{CH{:}C(C_6H_4{\cdot}OMe)}\end{array}{>}\mathrm{O}$, is prepared from anisaldehydecyanhydrin and anisaldehyde, methoxymandelamide being also formed; it crystallises from light petroleum in prisms, and melts at 145°. The *hydrochloride* melts and decomposes at 195°.

*β Phenyl-μ-propylphenyloxazole*,  $\mathrm{N}{<}\begin{array}{l}\mathrm{C(C_6H_4Pr)}\\ \mathrm{CH{=}CPh}\end{array}{>}\mathrm{O}$, obtained from cuminaldehyde and benzaldehydecyanhydrin, melts at 50°, and boils above 360°; the *hydrochloride* crystallises from alcohol in prisms, and melts at 152°.

*β-Methoxyphenyl-μ-propylphenyloxazole*,  $\mathrm{N}{<}\begin{array}{l}\mathrm{C(C_6H_4Pr)}\text{———}\\ \mathrm{CH{:}C(C_6H_4{\cdot}OMe)}\end{array}{>}\mathrm{O}$, is prepared from cuminaldehyde and anisaldehydecyanhydrin, and forms small needles which melt at 55°; the *hydrochloride* crystallises in needles, and melts at 160°.

*β : μ-Phenylstyryloxazole*,  $\mathrm{N}{<}\begin{array}{l}\mathrm{C(CH{:}CHPh)}\\ \mathrm{CH{=}CPh}\end{array}{>}\mathrm{O}$, produced from cinnamaldehyde and benzaldehydecyanhydrin, crystallises from light petroleum in clusters of needles, and melts at 62°; the *hydrochloride* melts at 125°.

*β-Methoxyphenyl-μ-styryloxazole*,  $\mathrm{N}{<}\begin{array}{l}\mathrm{C(CH{:}CHPh)}\text{—}\\ \mathrm{C{:}C(C_6H_4{\cdot}OMe)}\end{array}{>}\mathrm{O}$, arises from the action of cinnamaldehyde on anisaldehydecyanhydrin, and melts at 99—100°; the *hydrochloride* melts and decomposes at 175°.

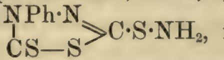
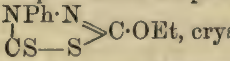
*β : μ-Diphenylimidazole*,  $\mathrm{N}{<}\begin{array}{l}\mathrm{CPh{\cdot}NH}\\ \mathrm{CH{-}CPh}\end{array}$, is formed when diphenyloxazole is heated at 300° with alcoholic ammonia for 6—7 hours, and crystallises from benzene in small, lustrous prisms, which melt at 162°; the *hydrochloride* melts and decomposes at 273°. It is also produced by the action of hydrogen chloride on a mixture of benzaldehyde and phenylamidoacetonitrile; the last-named substance, which has been hitherto known in the liquid form, crystallises from light petroleum in colourless leaflets which melt at 55°, whilst the *hydrochloride* crystallises from alcohol, and melts, decomposing, at 173°.

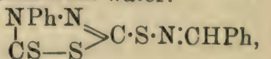
It has been shown (*loc. cit.*) that under the influence of chromic acid the oxazole ring is ruptured, and phenylglyoxylbenzamide produced; the action of chlorine is similar, the alcoholic solvent in presence of the halogen giving rise to an alkyl derivative.

*Phenylglyoxylmethoxybenzylamine*, OMe·CHPh·NH·CO·CPhO, is produced on passing chlorine into an ice-cold solution of $\beta : \mu$-diphenyloxazole in methylic alcohol; it crystallises from the latter solvent in small needles, and melts at 105°. *Phenylglyoxylethoxybenzylamine* is obtained when ethylic alcohol is employed, and crystallises in slender needles melting at 116°. The action of the halogen on $\beta : \mu$-diphenyloxazole dissolved in acetone, gives rise to phenylglyoxylbenzamide (*loc. cit.*).

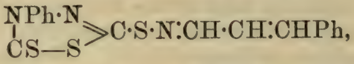
*Phenylglyoxylmethoxybenzamide*, OMe·$C_6H_4$·CO·NH·CO·CPhO, is formed when chlorine is passed into a solution of $\beta$-phenyl-$\mu$-methoxyphenyloxazole dissolved in acetone; it crystallises in slender prisms, and melts at 150°.

*Nitro-$\beta : \mu$-diphenyloxazole*, $C_{15}H_{10}O_3N_2$, is obtained by the action of cold, fuming nitric acid on $\beta : \mu$-diphenyloxazole, and crystallises from glacial acetic acid in beautiful, yellow needles, which melt at 185°; the substance is indifferent towards alkalis and chlorine, whilst oxidation with chromic acid gives rise to paranitrobenzoic acid, and a compound, which is probably the nitro-derivative of phenylglyoxylbenzamide. M. O. F.

**Derivatives of Hydrosulphamine.** By MAX BUSCH (*Ber.*, 1896, **29**, 2127—2143; compare Abstr., 1894, i, 625).—*Phenyldithiobiazolone hydrosulphamine*,  $\begin{array}{l}\text{NPh·N}\\ \,|\\ \text{CS—S}\end{array}\!\!>\!\text{C·S·NH}_2$, is obtained by the action of alcoholic ammonia on phenyldithiobiazolone bisulphide (*loc. cit.*), and crystallises from chloroform in transparent prisms; it becomes brown at 130°, and melts with effervescence at 136°. The *ammonium* derivative of phenyldithiobiazolone hydrosulphide crystallises from the mother liquor in silky needles, and melts above 200°, becoming yellow at 160°. When an alcoholic solution of the hydrosulphamine is boiled, ammonia is liberated, and the bisulphide regenerated, the same change occurring under the influence of dilute mineral acids; fusion gives rise to nitrogen and ammonia, along with phenyldithiobiazolone *tetrasulphide*, $(C_8H_5N_2S_2)_2S_4$, which crystallises from a mixture of chloroform and alcohol in small needles, and melts at 131—132°. Alcoholic potash readily dissolves phenyldithiobiazolone hydrosulphamine, ammonia being eliminated; on boiling the liquid, precipitation of potassium sulphite takes place, and *ethoxyphenyldithiobiazolone*,  $\begin{array}{l}\text{NPh·N}\\ \,|\\ \text{CS—S}\end{array}\!\!>\!\text{C·OEt}$, crystallises out in silky needles melting at 87—88° when the alcoholic liquid is diluted with water.

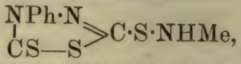
*Phenyldithiobiazolonebenzylidenesulphime*,  $\begin{array}{l}\text{NPh·N}\\ \,|\\ \text{CS—S}\end{array}\!\!>\!\text{C·S·N:CHPh}$, is produced on heating a mixture of phenyldithiobiazolone with benzaldehyde, in molecular proportion, on the water bath; it crystallises in slender, white needles, or thick, transparent plates, and both forms melt at 154—155°. Alcoholic hydrochloric acid converts the sulphine into the hydrochloride of benzylideneimide (compare this vol., i, 677), this substance being resolved into benzaldehyde and ammonium chloride under the influence of water, whilst an alcoholic solution deposits ammonium chloride, and then contains *benzylidene diethylic ether*, which melts at 180—181°, effervescing feebly.

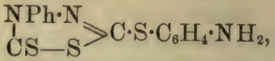
*Phenyldithiobiazolonecinnamylidenesulphime*,

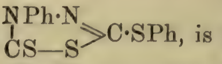


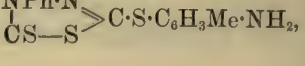
$$\left.\begin{matrix}\text{NPh·N}\\ |\quad\quad\\ \text{CS—S}\end{matrix}\right>C\cdot S\cdot N{:}CH\cdot CH{:}CHPh,$$

is prepared from phenyldithiobiazolone hydrosulphamine by heating it with cinnamaldehyde in alcoholic solution at 50—60°; it crystallises in slender, yellowish needles, and melts at 172—173°. Alcoholic hydrochloric acid converts it into *cinnamylideneimide hydrochloride*, which crystallises in lustrous needles or silvery leaflets, and is converted into a black mass at 170°; treatment with water produces ammonium chloride and cinnamaldehyde, whilst phenylhydrazine gives rise to cinnamylidenephenylhydrazone and ammonium chloride.

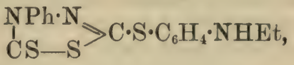
*Phenyldithiobiazolone methylhydrosulphamine*,  $\left.\begin{matrix}\text{NPh·N}\\ \text{CS—S}\end{matrix}\right>C\cdot S\cdot NHMe$, obtained by the action of methylamine on phenyldithiobiazolone bisulphide, crystallises in white needles which melt at 85°; *phenyldithiobiazolone ethylhydrosulphamine* forms lustrous, white needles, and melts without decomposing at 95—96°, whilst *phenyldithiobiazolone dimethylhydrosulphamine* is a yellowish oil. The *dimethylamine* derivative of phenyldithiobiazolone hydrosulphide is produced along with the latter substance, and crystallises in lustrous leaflets melting at 117—118°; the *methylamine* derivative is associated with the methylhydrosulphamine. The *trimethylamine* derivative of phenyldithiobiazolone hydrosulphide is obtained by the action of trimethylamine on the bisulphide, and crystallises in long prisms melting at 145—146°, whilst tripropylamine gives rise to the *tripropylamine* derivative, which melts at 126°.

*Phenyldithiobiazolone amidophenyl sulphide*,  $\left.\begin{matrix}\text{NPh·N}\\ \text{CS—S}\end{matrix}\right>C\cdot S\cdot C_6H_4\cdot NH_2$, obtained by the action of aniline on phenyldithiobiazolone bisulphide, crystallises from alcohol in colourless, lustrous leaflets melting at 163—164°; the *hydrochloride* forms slender, white needles, and undergoes dissociation at 194°; the *diazo*-compound is somewhat unstable, a solution evolving nitrogen at 60—70°; and the *azo*-compound crystallises from benzene in beautiful, lustrous needles, and melts at 218°. The *aniline* derivative of phenyldithiobiazolone hydrosulphide is produced along with the amidosulphide; it is very readily soluble in alcohol, and crystallises from a mixture of this agent with ether in slender needles, melting at 155°.

*Phenyldithiobiazolone phenyl sulphide*,  $\left.\begin{matrix}\text{NPh·N}\\ \text{CS—S}\end{matrix}\right>C\cdot SPh$, is produced from the amido-derivative, by means of the diazo-reaction and crystallises from dilute alcohol in lustrous leaflets.

*Phenyldithiobiazolone amidotolyl sulphide*,  $\left.\begin{matrix}\text{NPh·N}\\ \text{CS—S}\end{matrix}\right>C\cdot S\cdot C_6H_3Me\cdot NH_2$, is obtained from phenyldithiobiazolone bisulphide and orthotoluidine, and melts at 128°; paratoluidine and dimethylaniline are without action on the bisulphide.

*Phenyldithiobiazolone ethylamidophenyl sulphide*,



$$\begin{matrix}\mathrm{NPh{\cdot}N} \\ | \\ \mathrm{CS{-}S}\end{matrix}\!\!>\mathrm{C{\cdot}S{\cdot}C_6H_4{\cdot}NHEt},$$

is prepared from the bisulphide and ethylaniline; it crystallises from alcohol in white needles, and melts at 165°. The *nitrosamine* forms lustrous, white needles, and melts at 136—138°. M. O. F.

**Synthesis of Dioxyazine Derivatives.** By FRIEDRICH KEHRMANN and H. BÜRGIN (*Ber.*, 1896, **29**, 2076—2078; compare Abstr., 1894, i, 54).—Zinke and Hagen's dihydroxytoluquinone (Abstr., 1883, 1118) readily reacts with orthamidophenol hydrochloride in hot, aqueous solution to form *hydroxytoluphenoxazone;* this crystallises in brown-red, prismatic crystals, melts at 215—216°, and dissolves in concentrated sulphuric acid. Its solutions in benzene, alcohol, and acetic acid are yellowish-red, and do not fluoresce.

*Methyltriphenodioxazine*, $C_6H_4<\substack{N \\ O}>C_6HMe<\substack{O \\ N}>C_6H_4$, is obtained when hydroxytoluphenoxazone (1 gram) is heated with orthamidophenol hydrochloride (2 grams) and benzoic acid (20 grams) to the boiling point of the acid in a paraffin bath for one minute. When crystallised from toluene, it forms small, dark red crystals with a green, metallic lustre. Its benzene and toluene solutions are yellowish-red, and show a strong, green fluoresence. J. J. S.

**Conversion of Cinchonine into Cinchonidine.** By WILHELM KOENIGS and AUGUST HUSMANN (*Ber.*, 1896, **29**, 2185—2187).—The authors have obtained cinchonidine by heating pure cinchonine with amyl alcoholic potash for 15—16 hours. Only about 5 per cent. of the cinchonine is thus transformed, and it has not been definitely determined whether homocinchonidine is not formed at the same time. These facts agree with the assumption that cinchonine and cinchonidine are stereoisomerides.

A considerable portion of the cinchonine, on treatment with amyl alcoholic potash, is converted into bases which are readily soluble in ether; from these a zincochloride melting at 206° was obtained.

J. J. S.

**Ketones of the Tropine Group. V. An Isomeride of Cocaine.** By RICHARD WILLSTÄTTER (*Ber.*, 1896, **29**, 2216—2227).—From the cyanhydrin of tropinone, the ketone produced by the oxidation of tropine, a series of compounds isomeric with cocaine can be formed.

*α-Ecgonine*, $C_9H_{15}NO_3$, is formed on hydrolysing tropinonecyanhydrin with concentrated hydrochloric acid, or better, by transforming the cyanhydrin directly into the methylic salts of α-ecgonine, and subsequently hydrolysing the latter. It forms snow-white leaflets, tolerably soluble in hot water, more sparingly in cold water and in absolute alcohol, and insoluble in ether. Its aqueous solution gives a yellow precipitate with phosphomolybdic acid, and its solution in sulphuric acid, a permanent red coloration with potassium permanganate. When recrystallised from water, α-ecgonine contains 1 mol. $H_2O$, but when precipitated from its aqueous solution by means of alcohol $\frac{1}{2}$ mol. $H_2O$; when anhydrous, it melts and decomposes at 305°. On warming with lead peroxide and water, carbonic anhydride is immediately eliminated. The *platinochloride*, with $4H_2O$ or $5H_2O$, consists of orange-yellow cubes, readily soluble in hot water, and melting and decomposing at 223—224°. The *aurochloride*, with $1H_2O$, crystallises in amber-yellow prisms, readily soluble in water and alcohol, and melts and decomposes at 183—184°.

The *methylic salt of α-ecgonine*, $C_{10}H_{17}NO_3$, is prepared by saturating a mixture of methylic alcohol and α-ecgonine hydrochloride with hydrogen chloride; it forms colourless prisms melting at 114°, is easily soluble in water, ethylic and methylic alcohols, and in chloroform, tolerably soluble in benzene, less readily in ether, and very sparingly in light petroleum. The *hydrochloride* is readily soluble in water, and gives no precipitate with mercuric chloride; the *picrate* is tolerably soluble in hot water, but only slightly in cold water and in hot ethylic alcohol; it forms orange-yellow prisms melting at 189—191°; the *platinochloride*, with $2H_2O$, melts and decomposes at 204°; the *aurochloride* forms thin, glistening plates melting at 95—96°.

*Methyl-α-ecgonine methiodide*, $C_{10}H_{17}NO_3,MeI$, is formed on adding methylic iodide to a solution of methyl-α-ecgonine in methylic alcohol. It forms glistening needles melting at 201—202°, is readily soluble in water and in hot acetone, almost insoluble in ethylic acetate, and, on fusion with potash, yields dimethylamine. The *aurochloride* forms golden-yellow needles melting at 120°. The *aurochloride* of *α-ecgonine methochloride* is formed on treating α-ecgonine methiodide with silver chloride; it melts and decomposes at 212°.

*Benzoyl-α-ecgonine* is produced on treating α-ecgonine with benzoic anhydride; it is very soluble in hot water, and often forms supersaturated solutions; it crystallises with $\frac{1}{2}$ mol. $H_2O$, and melts and decomposes at 209°.

*α-Cocaine*, $C_{17}H_{21}NO_4$, is best formed by benzoylating methyl-α-ecgonine with benzoic chloride in benzene solution; α-cocaine hydrochloride then separates as an oil, from which the artificial alkaloïd is obtained by treatment with sodium carbonate, and is purified by recrystallisation from light petroleum; it forms long, transparent prisms, melts at 87—88°, is almost insoluble in hot and cold water, easily soluble, however, in most of the ordinary organic solvents, and has many of the properties characteristic of ordinary cocaine; it has, however, no effect physiologically. The *hydrochloride* forms needles and prisms, melts at 180°, and it is almost insoluble in water. The *hydriodide* forms glistening needles containing $1\frac{1}{2}$ mol. $H_2O$, and melts and decomposes at 192°. The *picrate* forms golden-yellow prisms melting at 195°; the *aurochloride* crystallises in thin plates, melting and decomposing at 222°; the *platinochloride* forms slender needles melting and decomposing at 220°.

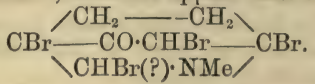
*α-Cocaine methiodide*, $C_{17}H_{21}NO_4,MeI$, consists of cubes containing 1 mol. $H_2O$, soluble in most hot solvents, excepting ether, in which it is insoluble in the cold, and melts at 202°. By boiling with soda, benzoic acid is obtained.

*α-Cocäthyline*, $C_{18}H_{23}NO_4$, is a heavy, colourless oil. The *aurochloride* forms yellow leaves melting at 188°, and is insoluble in cold water. The *platinochloride* separates from water in anhydrous plates melting and decomposing at 215°. J. F. T.

**Ketones of the Tropine Group. VI. The Action of Bromine on Tropinone.** By RICHARD WILLSTÄTTER (*Ber.*, 1896, **29**, 2228—2230).—Undiluted bromine reacts very energetically with tropinone, hydrogen bromide being eliminated in large quantities; the action is not so violent when the substances are dissolved in chloroform.

*Tetrabromotropinone*, $C_8H_9Br_4ON$, is formed by the prolonged action of bromine on tropinone hydrobromide, and is insoluble in water, concentrated hydrochloric acid, and alkalis, readily soluble in ether, benzene, acetone, and chloroform, also readily soluble in hot alcohol, ethylic acetate, and glacial acetic acid, whilst sparingly soluble in the latter solvents in the cold. It crystallises in pale yellow plates melting at 164°, and decomposing with elimination of hydrogen bromide at 190°. On oxidation with concentrated nitric acid, tetrabromotropinone yields *tribromopyridine*, $C_5NH_2Br_3$, which is purified by recrystallisation from pure nitric acid, from which it separates in long needles melting and decomposing at 167—168°. It is insoluble in water, readily soluble in hot alcohol, also in benzene, chloroform, ethylic acetate, and hot glacial acetic acid, but insoluble in cold hydrochloric acid and in light petroleum.

From its behaviour, on oxidation, it would appear that tetrabromotropinone has the constitution



$$\mathrm{CBr}\begin{array}{c}\diagup\mathrm{CH_2}\text{———}\mathrm{CH_2}\diagdown\\ \text{——}\mathrm{CO{\cdot}CHBr}\text{——}\\ \diagdown\mathrm{CHBr(?){\cdot}NMe}\diagup\end{array}\mathrm{CBr}.$$

J. F. T.

**Formation of ψ-Tropigenine.** By RICHARD WILSTÄTTER (*Ber.*, 1896, **29**, 2231).—If there is the same relation between tropigenine (the alcoholic base formed by the oxidation of tropine) and ψ-tropigenine (the isomeric compound produced by the oxidation and subsequent reduction of tropigenine), as between tropine and Liebermann's ψ-tropine, then ψ-tropigenine should be directly formed from ψ-tropine on oxidation.

By oxidising ψ-tropine, dissolved in aqueous potash, with potassium permanganate, ψ-tropigenine is undoubtedly produced, and can be identified by means of its carbamate melting at 140°, its orange-yellow aurochloride, melting and decomposing at 212°; and, finally, by means of its *n*-benzoyl derivative (m. p. 166°), prepared by Schotten's method. J. F. T.

**Chemistry of the Cactaceæ.** By ERVIN E. EWELL (*J. Amer. Chem. Soc.*, 1896, **18**, 624—643).—A summary of Lewin and of

Heffter's work on the alkaloïds derived from the various species of Anhalonium (compare Abstr., 1895, i, 120; this vol., i, 194, 267). The author has isolated two other alkaloïds from mescal buttons (*Anhalonium Lewinii*), one of which is more physiologically active than those previously obtained from these cacti. Details will be published later. J. F. T.

**Bebeerine or Bebirine.** By Max Scholtz (*Ber.*, 1896, **29**, 2054—2058).—Bebirine is readily obtained in an amorphous condition from commercial "bebeerinum purum" by extraction with ether. The yellow powder thus procured dissolves readily in methylic alcohol, but soon begins to separate rapidly and finally forms a pulp composed of small, colourless, shining prisms. The crystalline compound, on analysis, gave numbers in agreement with the formula, $C_{18}H_{21}NO_3$, given by Bödeker (*Annalen*, 1849, **69**, 54) and Flückiger (*N. Jahrb. Pharm.*, **31**, 257). When crystalline, it melts at 214°, and dissolves sparingly in alcohol, but after dissolution in acetone or chloroform separates in the amorphous condition and has the melting point, 180°, and other properties of that modification; it dissolves in hydrochloric acid, and the solution, on evaporation, deposits the *hydrochloride* in the form of bundles of small needles melting at 259—260°.

The behaviour of the substance towards nitrous acid proves that the base is a tertiary amine; when it is heated with methylic iodide, the *methiodide*, $C_{18}H_{21}NO_3,MeI$, is produced; this crystallises in slender, silky needles, and melts at 268—270°.

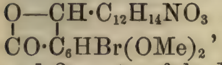
Bebirine contains no methoxy- or ethoxy-groups, but it dissolves in soda, thus evincing a phenolic character, which is further indicated by the behaviour of the base towards acidic anhydrides; when heated gently with acetic anhydride, a *monacetyl* derivative, $C_{18}H_{20}NO_3Ac$, is obtained; this melts at 147—148°, and is insoluble in soda, but dissolves readily in acids. The *benzoyl* derivative, $C_{18}H_{10}NO_3Bz$, prepared in a similar manner, melts at 139—140°. No aldehydic or ketonic group is present in bebirine.

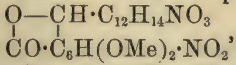
The base is oxidised if left in contact with alkaline ferricyanide during six hours, and then, the addition of ammonium chloride causes a precipitate of a basic *substance*, $C_{18}H_{19}NO_4$; the latter is sparingly soluble in alcohol, and chars when heated above 260°.

The alkaloïd is optically active, a 1·6 per cent. solution in alcohol having a rotation $[\alpha]_D = -298$. A. L.

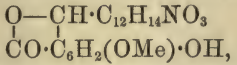
**Cuskhygrine.** By Carl T. Liebermann and Gustav Cybulski (*Ber.*, 1896, **29**, 2050—2051; compare Abstr., 1895, i, 310).—The author's statement that cuskhygrine affords little or no hygric acid on oxidation with chromic acid, is now proved to be erroneous; under altered conditions, a fairly good yield of the acid is obtained together with an oily substance, possibly a second acid, which gradually assumes a crystalline form, but is hygroscopic and difficult to purify.

The production of hygric acid from cuskhygrine is indicative of its derivation from a methylpyrrolidine. A. L.

**Derivatives of Isonarcotine.** By CARL T. LIEBERMANN (*Ber.*, 1896, **29**, 2040—2045; compare this vol., i, 264).—*Bromisonarcotine*,  $\begin{array}{l} O—CH\cdot C_{12}H_{14}NO_3 \\ CO\cdot C_6HBr(OMe)_2 \end{array}$, is obtained when 3 parts of bromopianic acid and 2 parts of hydrocotarnine are treated with sulphuric acid in a manner similar to that described in the first paper (*loc. cit.*). The base dissolves readily in alcohol, and crystallises therefrom on the cautious addition of water; it melts at 175°. Its hydrochloride and sulphate are sparingly soluble in cold water; unlike isonarcotine, when dissolved in sulphuric acid it gives only a feeble yellow coloration; its double salts with gold and platinum are obtained as flocculent, yellow precipitates. In order to ascertain whether it was derived from narcotine or isonarcotine, it was reduced with zinc dust and hydrochloric acid, and the base formed was liberated with ammonia the substance thus obtained had all the properties of isonarcotine.

*Nitroisonarcotine*,  $\begin{array}{l} O—CH\cdot C_{12}H_{14}NO_3 \\ CO\cdot C_6H(OMe)_2\cdot NO_2 \end{array}$, prepared from nitropianic acid and hydrocotarnine, crystallises from dilute alcohol in yellow needles, and melts and decomposes at about 205°. It dissolves readily in hydrochloric acid, and its solution in sulphuric acid is yellow.

*Methylnorisonarcotine*, $COOH\cdot C_6H_2(OMe)(OH)\cdot CH{:}C_{12}H_{13}NO_3$, or



$$\begin{array}{l} O—CH\cdot C_{12}H_{14}NO_3 \\ CO\cdot C_6H_2(OMe)\cdot OH, \end{array}$$

prepared from methylnoropianic acid and hydrocotarnine, is precipitated from its solution in dilute sulphuric acid, on adding excess of soda, as a sodium salt, from which the hydrochloride of the base may be obtained by means of hydrochloric acid. The free base dissolves sparingly in water, imparting to it a weak alkaline reaction; it is somewhat readily soluble in alcohol, and is deposited from hot benzene in crystals containing ½ mol. benzene of crystallisation, the greater portion of which is lost, in a desiccator over paraffin, in about 12 days. It melts and decomposes at 209°, whilst the freshly prepared benzene compound melts at 149—151°. It dissolves in concentrated sulphuric acid with the same red coloration as is observed in the case of isonarcotine, and its alcoholic solutions, with ferric chloride, give the beautiful blue coloration characteristic of hydroxy-compounds. The *sodium* salt of methylnorisonarcotine is insoluble in alcohol, but crystallises from boiling amylic alcohol. A solution of the base in dilute ammonia gives white precipitates of the calcium and silver salts on the addition of calcium chloride and silver nitrate respectively. The *hydrochloride*, *nitrate*, *sulphate*, and *picrate* of methylisonarcotine are all sparingly soluble in cold water, the first crystallising in small, white leaflets; the platinochloride,

$$(C_{21}H_{21}NO_7)_2,H_2PtCl_6,$$

is obtained as a yellow precipitate.

The production of the above compounds has induced the author to investigate the behaviour of aldehydes in general towards hydrocotarnine; benzaldehyde unites with the latter to form *hydroxybenzylhydrocotarnine*, $OH\cdot CHPh\cdot C_{12}H_{14}NO_3$; this crystallises from dilute alcohol, melts and decomposes at about 240°, and dissolves in sulphuric acid with the production of a feeble yellow coloration; it has a feeble alkaline reaction, yields a deliquescent hydrochloride, and an amorphous platinochloride and aurochloride; it is not affected by phosphorus oxychloride. Cinnamaldehyde reacts with hydrocotarnine in a similar manner. A. L.

**Scopolamine.** By ERNST SCHMIDT (*Ber.*, 1896, **29**, 2009—2014; compare Abstr., 1895, i, 158).—Replying to the criticism of Hesse (this vol., i, 655), the author points out that the substance described by Hesse as atroscine closely resembles the inactive scopolamine, which he has previously described, and which is formed by the action of alkalis on scopolamine hydrobromide. He proposes to institute a careful comparison of the two in order to decide the question. The inactive scopolamine has precisely the same physiological action as the active modification. A. H.

**Occurrence of Stachydrine in the Leaves of Citrus vulgaris.** By ERNST JAHNS (*Ber.*, 1896, **29**, 2065—2068).—The chief basic constituent of leaves of the bitter orange (*Citrus vulgaris*) is stachydrine, which has already been obtained from the tubers of *Stachys tuberifera* (compare von Planta and Schulze, Abstr., 1893, i, 447, 679). The free base crystallises with $1H_2O$, which it loses at 100°. Its *methylic salt*, $C_7H_{12}MeNO_2$, is obtained in the form of its *hydrochloride*, on saturating a methylic alcoholic solution of the base with hydrogen chloride and evaporating at the ordinary temperature. The *free ether* is readily decomposed; its *aurochloride* forms glistening plates, melts at 85°, and is more sparingly soluble than stachydrine aurochloride.

Stachydrine, when boiled with concentrated potash solution, yields dimethylamine, and its general properties agree with the formula $NMe_2{\cdot}C_4H_6{\cdot}COOH$. J. J. S.

**Urobilin.** By ARCHIBALD E. GARROD and F. GOWLAND HOPKINS (*J. Physiol.*, 1896, **20**, 112—143).—With the exception of Jaffe's method, which is difficult of application, the processes usually employed for the extraction of urobilin from urine are not calculated to yield a pure product. The method used in the present experiments consists in precipitating the pigment by saturating the urine with ammonium sulphate after it had been previously saturated with ammonium chloride to free it from urates. The pigment is then dissolved out from the precipitate by water, and reprecipitated with ammonium sulphate, this process being repeated several times; the final precipitate is dissolved in dilute ammonia, precipitated with a minimal excess of sulphuric acid, washed with saturated solution of ammonium sulphate, and freed from this salt by solution and resolution in absolute alcohol.

Another method used is to remove the urates by ammonium chloride, acidify with sulphuric acid, and saturate with ammonium sulphate. The urine so treated, yields its urobilin readily to solvents, of which a mixture of chloroform and ether (1 : 2) is recommended as the most selective; the ether-chloroform extract is then shaken with water to which a trace of alkali has been added, the pigment passing into solution in the alkaline water. This solution is once more saturated with ammonium sulphate, and the process of extraction with ether-chloroform repeated.

Urobilin, obtained from various human sources, that is, from normal and morbid urines, from fæces and from bile, is one and the same substance. Specimens from these several sources have, when pure, identical chemical and optical properties, and show in common a spectroscopic character which has not been previously described, namely, a second, narrow absorption band in the neighbourhood of the E line when the pigment is partially precipitated from an aqueous alkaline solution by acidification. The differences which have been described as existing between the different products are in part due to impurities in the specimens examined, and in part to the varying amounts of urobilin in the specimens. Urobilin is an unstable substance, and is liable to undergo certain modifications; these modified pigments have not the properties of the described pathological urobilins, and are capable of reconversion into the typical form. W. D. H.

**Absorption of the extreme Violet and Ultra-violet Rays of the Solar Spectrum by Hæmoglobin, its Compounds, and certain of its Derivatives.** By ARTHUR GAMGEE (*Proc. Roy. Soc.*, 1896, **59**, 276—279).—Compounds of hæmoglobin with oxygen, carbonic oxide, and nitric oxide present, even in highly dilute solutions, an absorption band between Fraunhofer's lines G and H. In the case of oxyhæmoglobin, the mean ray absorbed coincides with λ 414·0.

The absorption band of the compound of carbonic oxide with hæmoglobin is slightly displaced towards the less refrangible end of the spectrum, and the compound with nitric oxide behaves identically, the mean ray absorbed being λ 420·5.

By reduction, or by boiling in a vacuum, the molecule of dissociable oxygen is removed from oxyhæmoglobin, and the absorption then corresponds with λ 426·0.

The absorption of the extreme violet depends on the iron-containing moiety of the hæmoglobin molecule.

Very dilute alkaline solutions of hæmatin exert a general absorption of the ultra-violet and extreme violet, but present no trace of definite absorption.

The acid compounds of hæmatin exhibit an absorption band which is exactly on the boundary of the ultra-violet proper, and which extends further into the ultra-violet as the concentration of the solution increases.

Solutions of hæmochromogen (Stokes' reduced hæmatin) exhibit an intense absorption band between *h* and G in the same position as the CO-hæmoglobin band, but more intense, the mean's ray corresponds with λ 420·0.

The absorption of the extreme and ultra-violet by methæmoglobin indicates that the substance is the product of a partial decomposition of the oxyhæmoglobin molecule.

The band in the extreme violet (and ultra-violet), which is characteristic of hæmoglobin, in no respect depends on the iron in the molecule.

This conclusion is based; (1) on the fact that none of the compounds of iron have the properties of producing a definite absorption in the extreme violet, or the adjacent ultra-violet; (2) on the study of hæmatoporphyrin, a substance derived from hæmatin by the removal of the iron.

Acid solutions of hæmatoporphyrin of extreme dilution exhibit an absorption band between *h* and H. If the solution be slightly more concentrated, K is absorbed, and the absorption of the ultra-violet extends more and more with concentration. Alkaline solutions of hæmatoporphyrin absorb the same spectral region, but with greater intensity.

Neither bilirubin, hydrobilirubin, nor urobilin present any definite absorption band in the region of the spectrum in which the absorption bands of hæmoglobin and its derivatives occur. J. F. T.

**Relations of Turacin and Turacoporphyrin to the Colouring Matter of the Blood.** By ARTHUR GAMGEE (*Proc. Roy. Soc.*, 1896, **59**, 339—342).—Solutions of turacin in caustic soda or ammonia so dilute as to be almost colourless, absorb the extreme violet and ultra-violet rays of the spectrum in precisely the same way as highly diluted solutions of the acid compounds of hæmatin, the resemblance being so complete that it is impossible to distinguish from the photographs of the spectrum which substance has been employed (compare preceding abstract).

Turacoporphyrin, formed by the action of strong sulphuric acid on turacin, presents in the ultra-violet an intense absorption band identical with that of hæmatoporphyrin obtained by the action of concentrated sulphuric acid on pure hæmatin.

These facts point to the essential identity of turacoporphyrin and hæmatoporphyrin, and, when taken in connection with the identity of the ultra-violet spectrum of turacin and of the acid hæmatin compounds, seems to show that turacin contains the atomic group which is the cause of the extreme violet and ultra-violet absorption spectra exerted by hæmoglobin, its compounds and principal derivatives.

J. F. T.

**The Proteïds of Malt.** By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1896, **18**, 542—558).—On the extraction of malt with water, five distinct substances are produced, namely, a globulin, an albumin, and three proteoses. *Bynedestin* (malt globulin) is readily soluble in dilute salt solution, from which it is precipitated on the addition of water. This globulin contains 2 per cent. more carbon and 3 per cent. less nitrogen than edestin.

Leucosin is identical in composition and properties with that found in wheat, rye, and barley (this vol., i, 399, 455); it is intimately associated with diastase, and is partially precipitated from its solutions on saturation with sodium chloride or magnesium sulphate.

A *protoproteose* readily precipitated from its aqueous solution by alcohol, and a *protoproteose* less readily precipitated, were also obtained; the composition of the former is the same as that of leucosin, that of the latter is, however, different. The presence of a deuteroproteose and a heteroproteose was also detected.

*Bynin* is a proteïd soluble in water and in saline solutions; it forms about 1·25 per cent. of the malt.

A *proteïd*, insoluble in water, in salt solution, and in alcohol, was also isolated. The composition and properties of this proteïd were not determined. J. F. T.

**The Proteïds of the Potato.** By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1896, **18**, 575—582).—The proteïds of the potato consist of a globulin for which the name *tuberin* is proposed, and a proteose, the latter, however, occurring only in small amounts.

Tuberin is precipitated by saturating its solutions with sodium chloride, sodium sulphate, magnesium sulphate or amonïum sulphate. With acetic or nitric acids, a precipitate is given readily soluble in an excess of acid. Potassium ferrocyanide, and mercuric chloride, give no precipitate, but picric acid or tannic acid throw down the globulin. With the biuret, Millon's, and the xanthoproteïc tests, the usual reactions are given. Tuberin is soluble in very dilute saline solutions; when dissolved in a 10 per cent. sodium chloride solution it shows a somewhat variable heat-coagulation point, depending on the conditions under which it is tested; but in general a flocculent coagulum is formed on heating to 60—65°. Coagulation is, however, not complete until the solutions have been heated for some time at 80°.

J. F. T.

**Legumin and other Proteïds of the Pea and the Vetch.** By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1896, **18**, 583—609).—Peas and vetches contain the same proteïds, which are nearly, if not entirely soluble in 10 per cent. sodium chloride solution. The greater part of the proteïds consists of a globulin, Braconnot's legumin, which is readily precipitated on dialysing its salt solutions; with nitric acid, Millon's and Ademkiewic's reagents, it gives the usual proteïd reactions. With strong solutions of legumin, the biuret test gives a violet colour at first, which, onstanding, becomes crimson-red, similar to the colour produced by peptones.

The legumin from the vetch is not coagulated by heat, nor even rendered turbid by prolonged boiling of its strong solution. The legumin from the pea, however, is partly coagulated by heating strong solutions in a water bath and sets to a firm jelly after thus heating for some time, this being the only essential difference between them. Besides the legumin, the pea and the vetch contain another proteïd in small amount, either an albumin or a globulin, which is soluble in extremely dilute salt solutions; the solutions being coagulated when heated to 80°.

Further, a very little proteose is present in the extracts of both seeds.

J. F. T.

**Conglutin and Vitellin.** By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1896, **18**, 609—623).—The proteïd present in the almond and the peach-kernel is amandin and not conglutin or vitellin, which are the names usually associated with this substance.

*Amandin* is readily soluble in very dilute acetic acid, and is dissolved in hydrochloric acid with the development of a violet-blue coloration on standing; with the biuret test, and also with a mixture of glacial acetic acid and concentrated sulphuric acid, solutions of this globulin give a fine violet colour.

*Corylin* is the proteïd of the walnut (*Juglans regia*), and hazel nut. When dry, it is a heavy, snow-white powder which is quite insoluble in distilled water at 20° or at 40°; it is, however, readily soluble in a 10 per cent. solution of sodium chloride. With the biuret test, the usual violet colour is obtained; and with Millon's and the xanthoproteïn tests, the ordinary proteïd reactions ensue. When dissolved in concentrated hydrochloric acid, a violet-blue coloration develops on standing; with glacial acetic acid and concentrated sulphuric acid, solutions of corylin give a violet colour.

To the proteïds from the Brazil-nut (*Bertholletia excelsa*), and the oat-kernel are given the names *excelsin* and *avenalin* respectively.

Hemp (*Cannabis sativa*), squash (*Cucurbita maxima*), and castor bean (*Ricinus communis*), contain edestin.

Lupin (*Lupinus*) contains, as the principal proteïd, conglutin.

The sun flower (*Helianthus*) contains edestin, contaminated with Ludwig and Kromayer's helianthotannic acid. J. F. T.

**Leucinimide, a product of Hydrolysis of Proteïds with Boiling Acids.** By C. HEINRICH L. RITTHAUSEN (*Ber.*, 1896, **29**, 2109—2110).—In a work on the proteïds of grain, published in 1872, the author described leucinimide, $C_6H_{11}NO$, as occurring in the residue from the preparation of tyrosine, leucine, glutamic acid, and aspartic acid, obtaining it in woolly masses of needles. This substance is now shown to be identical with the pyridine derivative, $C_5H_7NO$, obtained by Cohn, on hydrolysing albumin with boiling hydrochloric acid (this vol., i, 658). M. O. F.

**Chemical Nature of Diastase. II.** By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, **18**, 536—542; compare this vol., i, 398).—Finely ground malt was treated with a solution of sodium chloride, and the filtrate saturated with ammonium sulphate; after filtration, the liquid was subjected to repeated dialysis into alcohol (0·86 sp. gr.). By this means, several fractions were obtained, which, after being further dialysed into water and then into alcohol, were dehydrated with absolute alcohol, and dried over sulphuric acid. The two middle fractions were found to be the most active, giving a diastatic power corresponding to 300. Only a small quantity of diastase was precipitated by bringing the alcohol-content of the malt extract to 50 per cent.

The purer the diastase is made, the more sensible it is to external conditions, and the method of testing the purity of the ferment by its maltose-producing power thus becomes of uncertain value. It is possible to roughly judge of the diastatic power of a preparation by heating a portion of its solution to 65°, and observing the amount of coagulate formed. J. F. T.

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